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A Temperature Variation Method to Assist in Vibrational Analyses of Complex Molecular Spectra

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A temperature variation method of determining the initial (lower) vibrational levels of the absorption bands of an electronic band system of a polyatomic molecule is presented. The determination is made from photometric measurements of the absorption at two temperatures not widely separated. Such absorption tube lengths are used that the absorption is everywhere much less than 100 percent in the bands to be studied. That variations in total absorption for a band may be measurable, the method is restricted to spectra in which the rotation lines are fairly broad compared with the intervals between them or else are very closely spaced. In such cases the rotational structure is blotted out on the photographic plate by the lack of resolution of the spectrograph and the exponential absorption law may be assumed in comparing absorption intensities at the two temperatures. A criterion is laid down for the applicability of the method in any instance. An equation is developed to give the heights (in cm^{-1}) of the excited vibrational levels of the normal electronic state involved in the various transitions, above that of some arbitrarily selected band of a group, as follows:

$$\log_{10}\rho_b/\rho_a=-0.623\left(\frac{1}{T_2}-\frac{1}{T_1}\right)(G_b-G_a)''.$$

The determination of the heights $(G_b-G_a)''$ in cm^{-1} comes from the two absolute temperatures and the ratio ρ_b/ρ_a of the heights of the absorption peaks on the two microphotometer traces.

INTRODUCTION

In the literature casual mention of the use of temperature variation to assist in the analysis of complex molecular absorption spectra is often found. The information that certain bands are associated with transitions from the normal state, while others occur from excited states whose heights above the normal state may be more or less closely estimated, may well bring order into an otherwise hopeless maze of frequencies. This information can be obtained from a systematic comparison of the relative changes in intensities of absorption of the different bands with temperature. A simple procedure applicable to a vibrational analysis in the photographic range will be presented here. The method is designed for use with closely spaced rotational structures appearing as unresolved band envelopes on the spectrum photograph. Its application could be extended to include molecules whose rotational structure can be blotted out by pressure.

The procedure is to seal off an appropriate mass of gas in an absorption tube and take plates of the absorption at two temperatures not widely separated. An extension is readily made to the investigation of a gas that dissociates under the energy of the continuous light source and must be flowed through the absorption chamber. To keep the same number of molecules in the light path under the two temperatures requires in this case an adjustment of pressure in conformity with the gas laws. The gas can be heated before admission to the tube and the pressure can be regulated by the valves controlling its rate of admission and exhaustion.

CRITERION OF APPLICABILITY OF THE METHOD

With N absorbing molecules in the light path, we have for gas absorption the exponential law

$$I=I_0e^{-\mu(\nu)N},$$

where $\mu(\nu)$ is the absorption coefficient of the material per molecule for frequency ν; I is the intensity of light of frequency ν transmitted by the gas and I_0 that incident on the gas chamber. This is the law for the ideal case of a single frequency under perfect resolution. But the absorption intensity of a line M is defined as $\alpha_M=\int_M\mu(\nu)d\nu$, and moreover plates of polyatomic vibration-rotation bands usually consist of partially resolved rotation lines. Under relatively high dispersion the rotational structure may be partially distinguishable while with low dispersion instruments only an envelope of unresolved structure is observed. In either event, since the absorption coefficient of the gas varies greatly in a very small frequency range among the band lines, the limits of usefulness of the exponential law must be examined.

In the spectrum of HCL, for example, in which the band lines are narrow compared with the intervals between them, this law cannot be expected to hold in gross. In infrared work Bourgin[1] showed that it is inapplicable to a single band line directly under ordinary working conditions. The apparent failure of the law was accounted for on the basis that the resolving power of the spectrometer with the slit widths used was not sufficient to give the true shapes of the absorption curves. In the type of spectrum for which the present method is proposed, namely, for closely spaced rotational lines, the slit width is large enough to include a number of lines. Thus much overlapping occurs on the spectrum photograph and the shapes of the individual absorption lines are completely blotted out. If the overlapping is sufficient the exponential law may now hold in gross, at least the gross effects may be comparable at two temperatures relatively close together.

If the rotation lines are broad compared with the distances between them, a small change of temperature will produce a measurable change in the intensity of absorption of the apparent band envelopes. Further, under such temperature variation the shapes of the rotation lines, hence of the envelope resulting from the overlapping, should not be sensibly altered provided the slit width remains the same. If the exponential absorption law is to be applicable, it is clear that the absorptions at all positions of maximum absorption coefficient, that is at the centers of the band lines, must be kept small compared with 100 percent (Dennison[2]). The validity of its application is subject to experimental check in any given case. Keeping the temperature constant, the absorption tube may be filled with the gas at two pressures such that the amounts of absorption are about the same as in the two spectrum photographs in which the temperature is varied. The criterion of applicability of the method is then that the heights of all peaks on the two microphotometer traces corresponding to the two pressures shall be proportional to these pressures.

When this criterion is obeyed, the necessity of using the technique employed by Bartholomé[3] (namely, broadening the band lines under pressure until little trace of the original structure remains) is avoided. It seems then that if the band lines either are naturally broad and diffuse or if they are so closely packed that the intervals between them are small the required conditions are fulfilled. This situation has apparently been encountered in the spectrum of sulphur dioxide (see paper following). It is to be expected that this will also be the case for a number of polyatomic molecules, while with other molecules the application of moderate pressure to the gas may make the absorption amenable to the criterion for the validity of the exponential absorption law.

The Photographic Plate and the Microphotometer

The theory of the method, involving the use of the microphotometer, will now be developed. The photographic plate, which is the basic element in the process, is discussed in a number of places.[4] "Density" may be represented on the straight line portion of a characteristic curve for a plate by

$$D=\gamma(\log_{10} E-\log_{10} i),$$

where γ is the "contrast factor," E (exposure) is the product It^s (I = intensity, t = time of exposure and s is the Schwarzchild constant), i is the "inertia" of the plate.

To write the density numerically it is necessary to find the ratio of two blackenings. By definition $D=\log (J_0/J)$, where J_0/J is the ratio of light coming through an unblackened part of the plate to that coming through the point under consideration. The microphotometer allows this evaluation. Fig. 1 is shown as illustration. The deflection of the galvanometer of the microphotometer, a, corresponding to an unblackened part of the plate, and the null deflection, i.e., the case of no light reaching the thermo-element, are marked, respectively, as A and D. The de-

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[1] D. C. Bourgin, Phys. Rev. **29**, 794 (1927).

[2] D. M. Dennison, Phys. Rev. **31**, 503 (1928).

[3] E. Bartholomé, Zeits. f. physik. Chemie **B23**, 131 (1933).

[4] G. R. Harrison, J. O. S. A. **19**, 267 (1929); L. S. Ornstein, W. J. Moll and H. C. Burger, *Objektive Spektralphotometrie* (Vieweg 1932); C. E. K. Mees, J. O. S. A. **21**, 573 (1931).

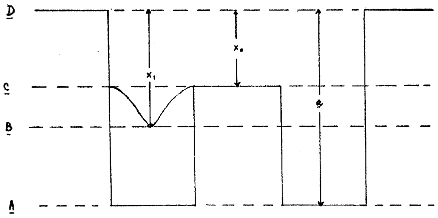

FIG. 1. *A*. Unblackened plate, i.e., complete absorption by gas. *B*. Partial absorption. *C*. Blackening by actual light source (no gas absorption). *D*. Complete blackening of photographic plate.

flections x_0, corresponding to the continuous source, and x_1, associated with a partial absorption, are shown at C and B, respectively. It may be assumed that small galvanometer deflections are proportional to the intensities of light incident on the thermopile of the microphotometer. Hence $J_0/J=a/x_0$ for the negative blackened by unabsorbed radiation from the continuous source, and $J_0/J=a/x$ for an adjacent region where the light of corresponding frequency has suffered selective partial absorption in a gas chamber.

Applying the exponential absorption law, which has been considered in the preceding section, for zero gas absorption we have

$$D_0=\gamma(\log I_0t^s-\log i)=\log (a/x_0);$$

for some gas absorption

$$D=\gamma(\log It^s-\log i)=\log (a/x).$$

Expanding D and substituting for $\log I_0$, we get

$$\mu(\nu)N=(1/0.43\gamma) \log (x/x_0),$$

provided x and x_0 both correspond to the straight line portion of the characteristic curve. The relation is not valid when x approaches complete absorption nor when x_0 is too small resulting from overexposure of the continuous source.

What is desired is to compare $N_\nu\mu(\nu)$ for two different ν's having in general a different number of absorbing molecules N_ν, where N_ν varies with temperature. For the frequencies ν_1, ν_2

$$(\mu N)_{\nu_2}/(\mu N)_{\nu_1}=\log (x_2/x_0)/\log (x_1/x_0).$$

If ν_1 and ν_2 show fairly weak absorption so that x_2/x_0 and x_1/x_0 are both not much greater than unity** then approximately

$$(\mu N)_{\nu_2}/(\mu N)_{\nu_1}=(x_2-x_0)/(x_1-x_0)=\rho.$$

If the temperature is varied by amounts which are small compared with the absolute temperature, the approximation is allowable.

POPULATION CONSIDERATIONS

Having seen the expression for the ratio of the absorption coefficients for two frequencies, now let us see what relation holds for a band envelope absorption at two temperatures. The relative absorptions of band lines depend on the relative populations of their initial states and on relative transition probabilities. The populations of the various states are given by the distribution law

$$N_1=(p_1/p_0)N_0e^{-Ghc/kT},$$

where N_0 is the number of molecules in the normal state and G is the energy in cm^{-1} of the state whose population N_1 is under consideration; p_0 and p_1 are the statistical weights, respectively. In the case that all vibrational levels are non-degenerate (as, e.g., with non-linear triatomic molecules), and if we are dealing with unresolved bands, so that N_0, N_1 stand for the total numbers of molecules in all the rotational levels of a given vibrational level, we may put $p_1=p_0$. Changes of N_1 with temperature allow the evaluation of G, and the problem is to determine these changes from the observed changes in intensity of absorption of the vibration bands.

Curtis and Darbyshire[5] in their work on the vibrational levels of the ICl molecule call attention to the importance of the changes of N_0 with temperature, which change had been neglected by previous workers. To avoid this difficulty they worked at constant pressure and arranged conditions to obtain equality of absorption for a particular band progression at two temperatures using the change of vapor density with temperature. In the present method this matter is taken care of in the computation rather than by an experimental procedure and so avoids the difficulties of adjustment associated with a null method. For in general comparing the intensities of two bands with initial states of energy (in cm^{-1}) G_a'' and G_b'', respectively, at the

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** In the expansion $e^y=1+y+\cdots$, if $y<<1$, then $\log e^y=e^y-1$, approximately.

[5] W. E. Curtis and O. Darbyshire, Trans. Faraday Soc. **27**, 77 (1931).

absolute temperatures T_1 and T_2, we have

$$R_a^{(1)}=N_a^{(T_1)}/N_0^{(T_1)}=e^{-G_a''hc/kT_1},$$

$$R_a^{(2)}=e^{-G_a''kc/kT_2},$$

$$R_b^{(1)}=e^{-G_b''hc/kT_1},\quad R_b^{(2)}=e^{-G_b''hc/kT_2}.$$

Let G_b'' be greater than G_a'' and T_2 greater than T_1. The heights of the absorption peaks will be represented by $x_a^{(T_1)}$, $x_a^{(T_2)}$, $x_b^{(T_1)}$, $x_b^{(T_2)}$ and the backgrounds corresponding to zero absorption of the continuous source $x_0^{(T_1)}$, $x_0^{(T_2)}$. The differences $x_a^{(T_1)}-x_0^{(T_1)}$, etc., are proportional then to the relative numbers of absorbing molecules.

$$\frac{R_a^{(2)}}{R_a^{(1)}}=\frac{x_a^{(T_1)}-x_0^{(T_2)}}{x_a^{(T_1)}-x_0^{(T_1)}}=\rho_a=e^{-(G_a''hc/k)(1/T_2-1/T_1)},$$

$$\frac{R_b^{(2)}}{R_b^{(1)}}=p_b=e^{-(G_b''hc/k)(1/T_2-1/T_1)},$$

$$\rho_b/\rho_a=e^{-(hc/k)(1/T_2-1/T_1)(G_b-G_a)''},$$

or

$$\log_{10}\rho_b/\rho_a=-0.623(1/T_2-1/T_1)(G_b-G_a)''.$$

That is, the differences of energy (in cm^{-1}) of the initial levels of the bands appear, so that the method may be applied to a group of bands at a time. Of the group, one is arbitrarily chosen for reference and the differences in energies between the initial levels of the other bands and that of the fiducial band can be computed. This is particularly valuable in studying bands coming from the higher initial levels, where the populations fall off rapidly with vibrational quantum number so that only part of the band system appears favorably on the photograph for a given pressure of gas in the absorption chamber. It is also convenient if a prism spectrograph with changing dispersion is used. Corrections between bands in different groups can then be determined by using exposures showing overlapping of adjoining groups. The case $G_a''=0$ is an important special case in the above.

PRACTICAL CONSIDERATIONS

Some fluctuation of the continuous source obviously is not of serious consequence in the two temperature pictures if the exposures are taken on the same plate and developed together with constant rocking. This procedure ensures that γ may be cancelled out in the computation as has been done above. According to Mees,[4] γ should be about $0.8\gamma_\infty$ for photometric work. For the galvanometer of the microphotometer to give large differences in deflection, the plate must not be very dense. Hence a shorter exposure and more prolonged development than is usual in spectroscopic work is indicated. Of course all plate blackenings must be on the straight part of the characteristic curve. Plates of medium speed are the most suitable giving a balance among latitude, contrast, speed and grain.

A small disturbance of the optical system between the two temperature exposures also does not invalidate the results obtained from the equation developed, inasmuch as a ratio of peak heights on the microphotometer traces is used. Likewise if between runs the microphotometer lamp changes slightly no serious damage is done although the lamp must remain constant during the course of any single run. However, if a long absorption tube is used, the light beam in the tube should be well collimated, since otherwise the change of refractive index of the gas with temperature will alter the cone of light so that the two plates may be of considerably different density. The optical arrangement may consist of a point source and an achromatic lens, or in the ultraviolet a long small bore hydrogen discharge tube used without a lens and with shields to limit the beam is quite satisfactory. If the intensity is sufficient, it is convenient to use no lens to focus the light emerging from the absorption chamber on the slit of the spectograph; if the light must be conserved an achromatic lens may be inserted to converge, but not focus it, in order that the spectrum shall be uniform across the slit.

Unfortunately in general the formula cannot be applied in a simple way over the whole band system due to overlapping of bands. In polyatomic spectra the complication that the band envelopes under investigation are the resultants of more or less closely overlapping vibration-rotation bands is common. Under this condition the ratios of intensities found for the absorption peaks will give apparent values of $(G_b-G_a)''$ as intermediate values which will depend on the relative strengths of the overlapping components. Nevertheless in some part of the spectrum a group of more or less unmixed peaks is likely to be found giving a clue to the proper assignment of the bands. Then the intermediate values of $(G_b-G_a)''$ serve as intensity checks on a proposed analysis.

If there exists a background of absorption from many unresolved weak bands or a continuous background which suffers temperature variation, only an examination leading to qualitative results may be feasible. Under such circumstances the line from which peak heights in the traces are measured (x_0) will have to be drawn from an appraisal of the condition present.

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On the Absorption Spectrum of Sulphur Dioxide

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An attempt to organize the absorption bands of sulphur dioxide in the region 3900–2600A has been made. The $(000)''-(000)'$ transition λ3129.5A (31,945 cm^{-1}) has been definitely located from a study of the temperature behavior of the lower frequency bands. Two of the vibrational frequencies known in the normal state have been observed and the intervals between successive lower levels determined. One of the frequencies in the excited state has been definitely assigned and a tentative value has been assigned for a second frequency. The configuration of the excited molecule is discussed.

Introduction

The spectrum of sulphur dioxide, a molecule known from its permanent dipole moment to be of triangular form[1] has attracted much attention. The normal modes of vibration of this type of molecule are well known.[2] If, as is very likely true of SO_2, the strong forces are those binding two atoms (here O) to a central atom (here S), the three frequencies can be classified as ν_2, a "deformation" frequency and ν_1 and ν_3, the symmetrical and unsymmetrical "valence" frequencies. The normal state of sulphur dioxide has been investigated from infrared and Raman data and the frequencies of the normal vibrations established with some certainty.[3]

Bands involving electronic transitions occur in the ultraviolet region of the spectrum and have been recognized as jumps to more than one excited electronic state. The more intensely absorbing higher frequency band system has been examined in emission and absorption by Chow,[4] in absorption by Jonescu[5] and at still higher frequencies by Wieland.[6] The lower frequency region, which is the subject of the present communication, has already been studied by Watson and Parker,[7] who arranged some of the observed absorption bands into series. These workers however used the older frequency for the ν_2 vibration of the molecule in the normal state; also they followed the formula for a diatomic molecule separately for the three modes of vibration, as has been pointed out by Dutta.[8] It thus seemed desirable to reexamine this portion of the spectrum. As a result of the present work, the $(0, 0, 0)''-(0, 0, 0)'$ band** has been located through detailed study of the temperature behavior of the various bands, using photo-

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[1] H. A. Stuart, Zeits. f. Physik. **59**, 13 (1929).

[2] D. M. Dennison, Rev. Mod. Phys. **3**, 180 (1931).

[3] For references see H. A. Stuart, *Molekulstruktur*, Springer, 1934.

[4] T. C. Chow, Phys. Rev. **44**, 638 (1933).

[5] A. Jonescu, Comptes rendus **197**, 35 (1933).

[6] K. Wieland, Nature **130**, 847 (1932).

[7] W. W. Watson and A. E. Parker, Phys. Rev. **37**, 1484 (1931).

[8] A. K. Dutta, Acad. Sci. U. P. India Bull. **1**, 89 (1931–32).

** A level of a molecule with three normal modes of vibration must be identified by three quantum numbers. These will be given in the order v_1, v_2, v_3, and that they belong to the excited or normal electronic state will be indicated by the prime and double prime, respectively.