always display some quadratic Stark effect which usually involves a shift of the frequency to longer wave-length. Sometimes, however, this Stark effect shift is to the blue, as, for example, in the 3933A and 3968A doublet of Ca II (the *H* and *K* lines) for which we observe at any pressure a blue shift of about 1/4 the amount of the red shift of the Al lines.

We wish to thank Dr. Dana T. Warren for his assistance during the early stages of this work.

APRIL 15, 1936 PHYSICAL REVIEW VOLUME 49

Note on Pressure Effects in Band Spectra

Henry Margenau, *Yale University*

(Received February 24, 1936)

A simple theory is presented describing pressure effects on band lines, insofar as they are due to foreign perturbing molecules without permanent polarity. Results are: Band lines are shifted and broadened much in the manner of atomic lines as a result of van der Waals interactions. Calculations with the models of a rigid rotator and a simple harmonic oscillator, for which formulas are given, show that the effects are practically independent of rotational and vibrational quantum numbers.

The effects of pressure on spectral lines are due, as is well known, to the interactions of the radiating particles with their neighbors. These interactions are of two main types: those which arise between similar systems, and those between dissimilar ones. The former are usually caused by optical resonance (except when both partners are unexcited), i.e., by the fact that a quantum of energy can be exchanged between the two agents in question; the magnitude of the perturbation is then proportional to the oscillator strength (f value) corresponding to the resonance transition. The latter type of interaction results from the mutual polarization of the partners; its magnitude depends on the f values of all possible transitions of both partners.

The phenomenon of "self-broadening," that is broadening by the same gas which emits or absorbs the line, is to be attributed principally to resonance interactions. It is particularly strong for atomic resonance lines, since their f values are large. Band lines, however, cannot be expected to exhibit this effect so markedly. For every electronic state of a molecule has a multiplicity of sublevels capable of combinations. The f value, which in the atomic case belonged to a single transition, is divided between several transitions, and the sharpness of resonance is thereby impaired. On the other hand, the second effect, which is evident in the broadening and displacement of lines by pressures of foreign gases, is of comparable magnitude in atoms and in molecules. It is to this effect that we wish briefly to call attention, since recent experiments by Watson and Hull[1] have yielded some quantitative information regarding it.

When a molecule in a state k is subject to the influence of a perturbing gas molecule having no dipole moment, and in its normal state, the system undergoes an energy change which is given by

$$\overline{\Delta E}=-\frac{2}{3R^6}\sum_{\lambda\kappa}{}'\frac{|(qr)_{0\lambda}|^2|(qr)_{k\kappa}|^2}{F_\lambda-F_0+E_\kappa-E_k},\qquad(1)$$

a formula which results from an application of the ordinary perturbation theory. F_0 is the energy of the normal state of the perturber (I), the E's are the energies of the excited molecule (II), qr denotes the dipole moment associated with a transition. The index λ labels the states of I, κ those of II. R is the distance between the particles, and the bar over ΔE indicates that an average over all orientations of molecule II has been taken. Formula (1) neglects the contribution of multipoles.

Since F_0 denotes the lowest energy of the perturber, all differences $F_\lambda-F_0$ are positive.

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[1] W. W. Watson and G. F. Hull, Jr., Phys. Rev., this issue.

Moreover, they are all large, of the order of a few electron volts, because it was supposed that molecule I has no dipole moment; for if rotational levels in the neighborhood of F_0 exist, their $(qr)_{0\lambda}$ would then vanish. The differences $E_\kappa - E_k$, on the other hand, may in general be either positive or negative. $\overline{\Delta E}$ may, in fact, have either sign. Hence band lines can show asymmetrical broadening and shifts to the red as well as to the blue.

The order of magnitude of the perturbation of band lines is the same as for atomic lines. Every $E_\kappa - E_k$ involves principally an electronic energy difference, with relatively small increments due to vibrational and rotational transitions superposed. If, for a rough approximation, we neglect the latter against the electronic parts of $E_\kappa - E_k$ and perform a suitable summation in (1) over these degenerate states, we are left with an expression in which the matrix elements in the numerators as well as the energies in the denominators are of the same general magnitude as they would be for atoms.

An abnormal situation of quasi resonance arises when some of the differences $E_k - E_\kappa$ are approximately equal to some $F_\lambda - F_0$. This case is more likely to occur with molecules than with atoms since the levels are spaced more closely and coincidence is more probable. Irregular perturbations may then be observed, to which the following considerations do not apply.

Let us now turn to the more interesting question of the dependence of the perturbations, and hence the line widths, upon rotational and vibrational quantum numbers. A reasonable answer to the first part of this question may be obtained by applying Eq. (1) to the interaction between a normal perturber and a rigid rotator of dipole moment μ. The matrix elements for the rotator and its energies are well known; if they are substituted in (1) and the summation over the degenerate states is performed, the result is

$$\overline{\Delta E_J} = -\frac{2}{3}\frac{\mu^2}{R^6}\cdot\frac{1}{2J+1}\left\{\sum_\lambda{}' |(qr)_{0\lambda}|^2 \times\left(\frac{J+1}{F_\lambda - F_0 - 2(J+1)B} + \frac{J}{F_\lambda - F_0 + 2JB}\right)\right\}, \quad (2)$$

where $B = h^2/8\pi^2 I$. The order of magnitude of this energy, which is to be added to the electronic perturbations just discussed, is found by neglecting the terms with B as compared to $F_\lambda - F_0$. Expression (2) then reduces to the classical interaction energy between a molecule of polarizability α and a dipole of moment μ, and becomes independent of J:

$$\overline{\Delta E} = -\frac{2}{3}\frac{\mu^2}{R^6}\sum_\lambda{}' \frac{|(qr)_{0\lambda}|^2}{F_\lambda - F_0} = -\frac{\alpha\mu^2}{R^6}. \quad (3)$$

For a dipole of moment $\approx 10^{-18}$, this energy is only about 1/20 of the electronic perturbation. The dependence on the rotational quantum number J is even more insignificant. The part of (2) which depends on J and which must be added to (3) is $-(\alpha\mu^2/R^6)\cdot 4J^2B^2/\overline{(F_\lambda - F_0)^2}$, as is seen by expanding (2) (neglecting smaller powers of J). The denominator of the last factor stands for some mean of $(F_\lambda - F_0)^2$; the last factor itself is thus completely negligible. A change in the width of band lines with rotational quantum number is therefore not to be expected as a result of the cause here considered.

A similar situation exists with regard to the dependence of this effect on the vibrational quantum number. An estimate sufficient for the present purposes may be derived by taking a simple harmonic oscillator in place of molecule II. With the use of the matrix elements for the oscillator in three dimensions, and upon averaging over all orientations, formula (1) finally reduces to

$$\overline{\Delta E_v} = (q^2 E_v / m\omega^2 R^6)\alpha. \quad (4)$$

Here α is again the polarizability of the perturbing molecule, E_v the energy and q the charge of the vibrator, while m and ω are its mass and its classical frequency. Perturbation (4) is still smaller than the effect given by (2) by a factor about 10, although the dependence on the vibrational quantum number v, contained in E_v, is more marked.

Theory predicts, therefore, that within attainable experimental accuracy the pressure of a foreign gas should shift and broaden all lines belonging to a given electronic transition similarly, and that they should react to foreign pressure approximately in the manner of the atomic line to which the transition corresponds as to type and energy.