

ON THE ESTIMATION OF MAXIMUM COEFFICIENTS
OF ABSORPTION

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ABSTRACT

On the basis of the correspondence principle it is shown that Einstein's coefficient of absorption can be estimated from the equation $B_{na} = 2\pi^2 e^2 Q^2 / 3h^2$ where e is the charge and Q the amplitude of the virtual oscillator which corresponds to the transition by absorption from state S_n to S_a . Assuming that probable maximum values can be obtained by taking e equal to the charge of one electron and Q equal to 3×10^{-8} cm, we obtain $(B_{na})_{\max} = 10^{20}$ in c.g.s. units, in agreement with values from 10^{14} to 2.3×10^{19} previously calculated by the author from absorption data.

IN connection with theories of the rates of chemical reactions, it is important to estimate the maximum values which we are likely to encounter for the coefficient of absorption of light by molecules.¹ The recent work of Van Vleck² on the form taken by the Bohr correspondence principle when applied to absorption, and of Hoyt³ and the present writer⁴ on the problem of the quantitative formulation of the correspondence principle, suggest a somewhat new approach to this question.

Consider two of the possible quantum states of a molecule, a lower (normal) quantum state S_n and an upper (activated) quantum state S_a , and let us investigate the passage of molecules from one of these states to the other by the absorption and emission of radiation. If we have N_a such molecules in the upper quantum state, the rate of spontaneous emission of energy due to the jump in question will have, on the basis of the *quantum theory*, the value

$$dR/dt = N_a A_{an} h\nu \quad (1)$$

where A_{an} is Einstein's coefficient giving the probability in unit time for the spontaneous emission of a quantum $h\nu$.

In order to apply the correspondence principle, let us now proceed in a manner which may for the moment seem somewhat arbitrary, and equate this rate of energy emission to the quantity

$$dR/dt = N_a (16\pi^4 e^2 / 3c^3) Q^2 \nu^4 \quad (2)$$

which is the rate of emission on the basis of the *classical theory* of a set of

¹ See for example Tolman, J. Amer. Chem. Soc. **47**, 1524 (1925).

² Van Vleck, Phys. Rev. **24**, 330 (1924).

³ Hoyt, Phil. Mag. **46**, 135 (1923); *ibid*, **47**, 826 (1924).

⁴ Tolman, Phil. Mag. **49**, 130 (1925).

harmonic electric oscillators of charge e , frequency ν , and amplitude Q . We obtain for Einstein's coefficient of spontaneous emission the expression

$$A_{an} = (16\pi^4 e^2 / 3hc^3) Q^2 \nu^3 \quad (3)$$

and by substituting the known relation

$$A_{an} = (8\pi h \nu^3 / c^3) B_{na} \quad (4)$$

between Einstein's coefficients of absorption and emission can obtain for the coefficient of absorption the expression

$$B_{na} = (2\pi^3 e^2 / 3h^2) Q^2 \quad (5)$$

where the desired quantity B_{na} is the chance per unit time that a molecule in state S_n will pass to the upper state S_a by absorption, when in the presence of radiation of unit density.

On the basis of the *correspondence principle*, however, we should expect the amplitude Q , which was introduced above in a seemingly artificial manner, to be calculable as an average of the corresponding amplitude present in the classically allowed motions of the molecule, which lie between the two quantum states S_n and S_a . Different methods of taking this average have been studied by Hoyt and the present writer, and the exactly correct method has not yet been determined. Nevertheless, since in accordance with Bohr's correspondence principle Q is the amplitude of that particular harmonic in the internal motion, having order numbers $\tau_1 \dots \tau_s$ equal to the changes in quantum numbers $\Delta n_1 \dots \Delta n_s$ which characterize the quantum transition in question, we should expect that a reasonable estimate of the probable maximum values of B_{na} could be obtained by taking Q of the order of molecular dimensions.

As a matter of fact, giving Q the value of 3×10^{-8} cm and assuming the charge e of the oscillating system to be that of one electron, we obtain from Eq. (5) the value $B_{na} = 10^{20}$ c.g.s. units. It is interesting to compare this estimated maximum with the values of B_{na} calculated by the author⁵ from actual absorption measurements in a variety of cases where data were available. The values obtained ranged all the way from 10^{14} to 2.3×10^{19} c.g.s.u., which are not out of accord with the above estimate.

In connection with the foregoing treatment, attention is called to the advantage obtained by using Eq. (5) to estimate possible values of B_{na} , rather than Eq. (4) to estimate values of A_{an} , since in this way we obtain a quantity which is independent of the frequency. This new possibility was suggested to the writer by Van Vleck's work.

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⁵ Tolman, Phys. Rev. **23**, 699 (1924).