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THE ISOTOPE EFFECT ON BAND SPECTRUM INTENSITIES

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Abstract

Theory of the isotope effect on intensities.—It is shown that there is no change in the electronic part of the transition probability with nuclear mass, and that the vibrational part is the only part that does show an effect. This effect is calculated on the basis of Hutchisson's expressions for the vibrational transition probability. The effect of a change in nuclear mass on the population of the initial state is also found if this population is given by the simple Boltzmann distribution.

Application of the theory to specific cases.—The magnitude of the isotope effect is found for certain bands of O_2, NO, and Cl_2 which have been used recently to measure the abundance of the isotopes of these substances by means of their band spectrum. The effect is small, being ordinarily less than ten percent, but it can not generally be neglected.

THE recent work of Babcock,[1] King and Birge,[2] and Naudé[3] on the isotopes of oxygen, carbon and nitrogen has opened up the question of whether or not the transition probability of a given line is different for two isotopic molecules. The only method available at present for finding the relative abundance of the isotopes of these elements, a matter of great importance in the case of oxygen as it is used as the basis for the atomic weight scale, is to compare the intensities of corresponding lines from the different isotopic species. Giauque and Johnston[4] have suggested that at least for symmetrical molecules like O_2 and C_2 it is possible that when the two component atoms are different isotopes the electric moment of the molecule would be greater than when both atoms are of the same weight, thus giving the lines of the unsymmetrical molecules a greater transition probability so that relative abundances estimated directly from intensities would be somewhat in error. This effect can be shown to be negligible, but obviously the whole matter needs discussion, and it is the purpose of the present paper to consider the possible effects of a difference in nuclear mass on the probabilities of transition between molecular states so as to make a more precise correlation between observed intensities and relative abundances possible. The isotope effect on the population of the initial state will also be considered for the cases where this population is given by the simple Boltzmann distribution. In the case of emission bands there are problems of differential excitation and possible effects of re-absorption, but as these can only be discussed in connection

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[1] H. D. Babcock, Proc. Nat. Acad. Sci. **15**, 471 (1929); Phys. Rev. **34**, 540 (1929).

[2] A. S. King and R. T. Birge, Astrophys. J. July (1930).

[3] S. M. Naudé, Phys. Rev. **36**, 333 (1930).

[4] Giauque and Johnston, Jour. Am. Chem. Soc. **51**, 1436 (1929) and **51**, 3528 (1929) Cf, esp. p. 1439.

with the exact arrangements of a given experiment they will not be taken up here. To summarize the results it turns out that for bands with low quantum numbers and if the difference of equilibrium nuclear separation for the two states is small, there will be small effects; for large quantum numbers and large difference in r_e there will be large effects on the intensity. These general results will then be applied to various actual cases.

Since intensity measurements are most easily controlled when made on absorption lines we shall consider the effect of nuclear mass on absorption coefficients, though the results on transition probabilities can be applied directly to emission lines also. The effects we are looking for must be well over one percent to be appreciable as the accuracy of most intensity measurements is not under ten percent. However, as small corrections from different effects are likely to add up to give a large correction in the end, we shall consider all corrections which are greater than one percent.

The absorption coefficient, α_{ij} for the transition $i\rightarrow j$ (where i and j symbolize all the quantum numbers) is given by

$$\alpha_{ij} = \text{const. } b_i \nu_{ij} [P_{ij}]^2 \tag{1}$$

ν_{ij} is the frequency of the line, b_i is the Boltzmann factor giving the population of the initial state and $P_{ij} = \int P\psi_i\psi_j d\tau$, P being the electric moment of the molecule as a function of the coordinates of the electrons and nuclei and the ψ's are the wave functions of the two states.

We are interested in the way in which α changes with the nuclear mass, so that all the factors which are independent of the nuclear mass have been put into the constant. ν_{ij} will vary slightly with mass, but ordinarly the isotopic frequency shift is very small compared to the whole frequency so that the effect of this can be neglected, and we can confine our attention to P_{ij} and b_i.[5]

Turning to P_{ij} we must find out first what the isotope effect on the ψ's will be. The wave function of a molecular state can be approximated by the product of two wave functions, $\psi^e\psi^n$ of which ψ^e is the wave function for the motion of the electrons when the nuclei are held fast and ψ^n is the wave function for the motion of the nuclei assuming them to be bound by a force function equal to the total energy of the molecule for the fixed nucleus case. (This total energy is a function of the nuclear separation). Obviously ψ^e does not depend on the nuclear mass and so if this product is a sufficiently good approximation to the real wave function, we can confine our attention to ψ^n. Kronig,[6] on the basis of some work of Slater[7] has worked out the coefficient of the correction term which should be added to the product $\psi^e\psi^n$ to give a more accurate expression, and he finds that it will be very small

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[5] In the case of emission the intensity depends on the fourth power of ν_{ij} so that the effect would be greater and in extreme cases might be appreciable.

[6] R. de L. Kronig, Zeits. f. Physik., **50**, 347 (1928) esp. p. 353 ff$_1$ I am indebted to Prof. E. C. Kemble for pointing out the connection between separability and perturbations.

[7] J. C. Slater, Proc. Nat. Acad. Sci. **13**, 423 (1927), also Born and Oppenheimer, Ann. d. Physik. **84**, 457 (1927).

(of the order of magnitude of the ratio of the electronic to the molecular mass) unless there is another state of a different electronic level which is very close to the state in question, and which can interact with it; in short, unless the level in question is perturbed.[8] Consequently we may say that the wave function is separable to a high degree of approximation under ordinary circumstances and we can confine our attention to ψ^n. This means also that the effect suggested by Giauque and Johnston[4] will be negligible ordinarily, as the electronic moment will not change appreciably between isotopic molecules even in cases like O_2 which are symmetrical.[9]

In discussing the isotope effect on ψ^n we can neglect the rotational part of the wave function because the rotational contribution to the transition probability is simply a function of the angular momentum quantum numbers and does not depend on the mass of the rotator so that the integrals involved in P_{ij} reduce to integrals of the two vibrational wave functions only, and are readily calculable.

Hutchisson[10] has calculated these integrals using the wave functions of a simple harmonic oscillator. He considers them to be applicable only to symmetrical molecules, but they are of more general applicability than he states as the following argument shows. We are dealing with integrals of the type

$$\int P\psi_i^e\psi_i^n\psi_j^e\psi_j^n d\tau$$

where P and the ψ^e's are functions of the coordinates of the electrons *and* the nuclei; the ψ^n's depends on the nuclear coordinates only. If we integrate over the electronic coordinates there remains

$$\int P_{kk'}(r)\psi_i^n\psi_j^n d\tau$$

where k and k' are the electronic quantum numbers of the states i and j respectively and $P_{kk'}(r)$ is a sort of electronic electric moment and is a function of the nuclear coordinates, that is to say of r, as we are considering vibration only. $P_{kk'}(r)$ can be expanded in a Taylor's series about some convenient point and the integrals calculated for each term in the series. Since ordinarily $P_{kk'}(r)$ changes with r very slowly compared to the ψ^n's and since it does not change very much in the region for which the ψ^n's are appreciable it turns out that "for low quantum number" the constant term in the expansion of $P_{kk'}(r)$ gives the largest contribution to the integral and the others can be neglected.[11]

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[8] Kronig's calculation can be greatly simplified if it is carried through in the original cartesian coordinates. The Euler's angles analysis is not necessary for this separability proof.

[9] By the same reasoning we can see that the molecule $O^{16}O^{18}$, for instance, will have a very small permanent electric moment and hence the pure rotation and the vibration-rotation bands in the infrared will be exceedingly faint—too faint to be ordinarily detectable.

[10] Elmer Hutchisson, Phys. Rev. **36**, 410 (1930).

[11] Cf. "Quantum Mechanics" Condon and Morse. McGraw-Hill 1929. p. 169 for a discussion of this subject. The fact that higher terms in the Taylor's expansion are negligible at least for low quantum numbers can be verified by direct calculation quite readily.

This reasoning is independent of whether or not the molecule is symmetrical, so that Hutchisson's formulas can be applied quite generally.

As the formulas for the integrals in the lower states are quite simple, we shall reproduce them here in a notation more suited to our problem. Using ω' and ω'' for the frequencies of vibration in the upper and lower states respectively, $\omega=\omega'+\omega''$, $B=h^2/8\pi^2I''C$ (where I'' is the moment of inertia of the molecule in the lower state) and $\zeta=(r'-r'')/r''$ and $\beta=(\omega'\omega''/4B\omega)\zeta^2$, they are [12,13]

$$\begin{aligned}
I_{00} &= \left(\frac{2(\omega'\omega'')^{1/2}}{\omega}\right)^{1/2} e^{-\beta} \\
I_{01} &= \frac{\omega''}{\omega}\left(\frac{\omega'}{B}\right)^{1/2} \zeta\left(\frac{2(\omega'\omega'')^{1/2}}{\omega}\right)^{1/2} e^{-\beta} \\
I_{02} &= \frac{1}{2^{1/2}}\,\frac{\omega'}{\omega}\left(\frac{2(\omega'\omega'')^{1/2}}{\omega}\right)^{1/2} e^{-\beta}\left(1-\frac{\omega''}{\omega'}+\frac{\omega''^2\zeta^2}{\omega B}\right) \\
I_{11} &= \frac{(\omega'\omega'')^{1/2}}{\omega}\left(\frac{2(\omega'\omega'')^{1/2}}{\omega}\right)^{1/2} e^{-\beta}\left(2-\frac{\omega'\omega''}{\omega}\,\frac{\zeta^2}{B}\right).
\end{aligned} \tag{2}$$

To find the isotope effect on the transition probabilities we need to find the effect of a change of nuclear mass on the expressions in Eq. (2). In calculating this we use the fact that the electronic part of the wave function is not affected by the nuclear mass, so that the "shape" of the nuclear binding potential will be the same in two isotopes. Hence ζ is unaffected by a change in nuclear mass, and the ω's will vary inversely as the square root of μ, the reduced nuclear mass. B, of course, varies inversely as μ. It is therefore a simple matter to see how any of the expression's in Eq. (2) will vary with μ In particular if ζ is large, so will be β, and the exponential will vary rapidly with μ. Also in this case the ruling term in the polynomial will be one in $(\omega/B)^{V'+V''/2}$ which will vary as $(\mu)^{V'+V''/4}$. However if ζ is small no definite statement can be made about which will be the ruling term and we can only say that the exponential will change slowly with μ. In general, therefore, we would expect large effects for transitions between states whose r_e's differ considerably (i.e. large ζ) and for large vibrational quantum numbers, but this is not an exact rule and each case must be examined separately to see what the effect will be. It should be noted also that for very large vibrational quantum numbers, especially when ζ is large also, the higher terms in the expansion of the electric moment will no longer make a negligible contribution to the intensity and a more general calculation will be necessary.

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[12] The constants ω', ω'', B and ζ are not necessarily ω_e B_e and ζ_e. We can go a long way toward taking account of the anharmonic character of the vibration by using ω_v, B_v and ζ_v instead.

[13] Unfortunately Hutchisson has used the wrong normalization coefficients so that the quantity which he calls C_3 should be (using his notation) $C_3=(2/\alpha(1+\alpha^2))^{\frac{1}{2}}e^{-\delta^2/2(1+\alpha^2)}$. This correction is of no importance in the calculations he makes as he is interested only in relative values, but where we are interested in dependence on mass it is necessary.

There is one other factor in the expression for α which depends on μ and that is the Boltzmann factor b. This factor is

$$b_i = \frac{e^{-E_i/kT}}{\sum\limits_i e^{-E_i/kT}} \tag{3}$$

where E_i is the energy of the ith state, k is the ordinary gas constant and T the absolute temperature. For the rotational levels of a molecule $E_K = hcBK^2$ where K is the rotational quantum number (we do not need to bother about the refinement of using $K(K+1)$ in this case) and B has the same significance as in Eq. (2). Since hcB is small compared to kT, the denominator of Eq. (3) can be considered as the integral $\int e^{-hBK^2c/kT}dK$ and so we can readily evaluate the rate of change of b_K with μ, getting

$$\frac{1}{b_K}\,\frac{db_K}{d\mu}\Delta\mu = \left(K^2\frac{B}{T}\,\frac{hc}{k} - \frac{1}{2}\right)\frac{\Delta\mu}{\mu}\,\cdot \tag{4}$$

For low rotational quantum numbers the first term in the parenthesis is small at ordinary temperatures so that the effect of μ on the population of the state will be one half the percentage change in μ. For lower temperatures or higher quantum numbers the effect will be smaller than this as shown by Eq. (4).

For the case of vibration the energy difference between successive levels is large and if the temperature is not too high, practically all of the molecules will be in the lowest state, in which case the summation in the denominator can be replaced by the first term of the sum only. In this case $E_v = h\omega_v(v+\frac{1}{2})$ so that we have

$$\frac{1}{b_v}\,\frac{db_v}{d\mu}\Delta\mu = v\frac{\omega_v}{T}\,\frac{hc}{k}\,\frac{\Delta\mu}{2\mu} \tag{5}$$

where v is the vibrational quantum number.

It is evident from this formula that there will be no isotope effect on the population of the lowest state ($v=0$), but there will be an effect on the population of higher states. It should be emphasized, however, that this formula can be applied only when the population of the excited states is absolutely negligible compared to that of the normal state. If this condition is not fulfilled the calculation is more elaborate.

Having discussed the possible sources of isotope effect on intensities we now turn to actual cases to apply our results.

In the case of oxygen, the measurements of abundance so far made are those of Babcock[1] on the atmospheric bands of O_2 and of Naudé[3] on the γ bands of NO. Babcock measured a number of individual lines in the 0-0 band and found the intensity ratio to be one in 1250, but he does not give a probable error. However we may safely assume it to be over ten percent. For these bands the quantity ζ is very small indeed and a simple calculation using the first formula of Eq. (2) shows that the transition probability for the $O^{16}O^{18}$ molecule does not differ by more than 0.2 percent from that for $(O^{16})_2$. As the bands were due to transitions from the lowest vibrational state there is no correction due to the vibrational Boltzmann factor, but the lines with low rotational quantum number will show an effect due to the rotational Boltzmann factor. This turns out to be about 2 percent for the lowest lines, but as Babcock used quite a number of lines for his measurement the average effect for all the lines will be less than this, so that, in view of the size of the experimental error, we can neglect the correction.[14]

Naudé's abundance estimate is based on the relative intensity of heads from the 1-0 band of the γ system of NO observed in absorption. The resolution was not sufficient to separate the lines so that they could be worked with separately, but the intensity of the heads as a whole was measured. A maximum error of about ten percent is given. In this case a calculation based on the second equation of Eqs. (2) shows that the transition probability for $N^{14}O^{18}$ is less than that for $N^{14}O^{16}$ by two percent.[15] The rotational Boltzmann factor correction for the P_1 heads can be readily calculated from Eq. (4) using $\beta = 1.70$ and $K = 11$ for the quantum number of the lines at the head,[16] and a correction of 2.7 percent is found in the opposite direction to that for the transition probability. As the two corrections cancel, it is evident that the intensity ratio gives the abundances directly.

The work of King and Birge[2] on carbon has not resulted in any numerical value of the abundance of the new isotope; in fact they report very anomalous behavior of the intensities which is as yet quite unexplained. There is therefore no point in calculating a numerical correction, but it can be said that the correction for the 0-1 band of the Swan system, which they have used so far, would be about one percent.

We now turn to the case of chlorine. Elliott[17] has measured the intensity ratio of lines from the molecules Cl^{35} Cl^{37} and $(Cl^{35})_2$ and has found a ratio different from that obtained from chemical data. The bands he has used are the 1–12, 2–12 and 2–6 bands in the visible absorption spectrum of Cl_2, and his figure for the relative intensity is 1.40,[18] whereas the chemical atomic weight in conjunction with the known weight of the two isotopes,[17] shows that the relative abundance of the two types of molecules is 1.59 leaving a discrepancy of 14 percent. Now chlorine is a case where we would expect a large isotope effect because of the large difference in r_e for the two states, and a calculation based on Hutchisson's results for the 2–6 band shows that the transition probability is different by 19 percent in the two kinds of

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[14] In this case there is no question of the levels being perturbed by being near other levels. Babcock's analysis of the band shows that. C.f. also Dieke and Babcock, Proc. Nat. Acad. Sci. **13,** 670 (1927).

[15] One might expect perturbations in this band because it lies on top of the $1-0$ β band, but no perturbations have been found (Jenkins and Rosenthal, Proc. Nat. Acad. Sci. **15,** 382 (1929)) so that we can be pretty sure there will be no trouble about separability in this case.

[16] C.f. R. Schmid, Zeits. f. Physik. **64,** 84 (1930).

[17] A. Elliott, Proc. Roy. Soc. **A123,** 629 (1929) and **A127,** 638 (1930) also Nature **126,** 133 (1930).

[18] Elliott corrects his measured ratio (1.35) to allow for the maximum possible effect of overlapping lines. 1.40 is obtained by using one half of that correction.

molecules. In applying Hutchisson's results to this transition a considerable simplification is possible because as ζ is fairly large, only one of the terms in the summation is appreciable. Further, this calculation was carried out using r_v and ω_v rather than r_e and ω_e. The 6th state of the upper level is markedly anharmonic and so it seemed of interest to carry out the calculation of the electric moment matrix using Morse's[19] wave function for the upper state and the harmonic wave function for the lower state. The calculation in this fashion is fairly long-winded but the result is similar to that from the harmonic analysis, the isotope correction to the transition probability being 15 percent. No attempt was made to calculate the corrections for the 1–12 or the 2–12 transition, but they will probably be of the same general magnitude as that for the 2–6 transition. Since the bands were due to transitions from the 2nd level we should look to the vibrational Boltzmann factor for an effect, and a simple calculation shows that the heavier molecule will have 7 percent greater probability of being in the second state than the light one.[20] This is in the opposite direction from the 15 percent found for the difference of transition probabilities so the correction to Elliott's abundance ratio is 8 percent, making the corrected figure 1.29, which differs from the chemical value by 22 percent. It is not possible to say whether or not this discrepancy is within the experimental error of the measurements as Elliott does not give an estimate of his error, but it seems larger than one would expect.

In this connection it is interesting to note that Meyer and Levin[21] measured the relative abundance of the chlorine isotopes from the infrared bands of HCl and obtained good agreement with the chemical value. The intensity ratio needs no correction in this case as the difference in μ between the two kinds of molecules is only a few tenths of one percent, and the probable experimental error is about twenty percent.

There are many other cases where bands due to two or more isotopic molecules have been observed, but, as in most of these cases the chief interest is in frequencies, the intensities are only estimated from the plates by eye and there is no point in applying the comparatively small isotope correction to these results.

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[19] P. M. Morse, Phys. Rev. **34**, 57 (1929).

[20] The rotational Boltzmann factor correction will be negligible in this case, because lines with relatively large rotational quantum numbers were used.

[21] C. F. Meyer and A. A. Levin, Phys. Rev. **34**, 44 (1929).