Errata: Vibrational Intensities. I. Theory of Diatomic Infra-Red Bands

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TABLE I. Isotope abundances[a] of krypton with different scanning methods.

Mass	Magnetic scanning							Electro-static scanning[b]
	750v	1000v	1500v	2000v	3000v	4000v	5000v	
78	0.350	0.347	0.351	0.353	0.357	0.354	0.358	0.39
80	2.26	2.27	2.27	2.29	2.33	2.32	2.31	2.52
82	11.62	11.63	11.61	11.55	11.55	11.59	11.58	12.03
83	11.51	11.57	11.54	11.47	11.48	11.52	11.51	11.64
84	56.76	56.93	56.96	57.10	56.99	56.90	56.99	56.80
86	17.48	17.25	17.29	17.25	17.30	17.31	17.28	16.62

[a] The abundances have all been corrected for the fact that with the capillary leak used the ratio of the partial pressures of two isotopes in the ion source differs from that in the sample by a factor depending on the square root of the mass ratio. (For a full discussion of this correction see M. G. Inghram, *Advances in Electronics*, Vol. I. (Academic Press, New York, 1948).)
[b] Magnetic field such that mass 78 is focused at 1700 volts ion accelerating potential.

TABLE II. Comparison of various isotopic krypton abundances.

Mass	This research	Nier[a]	Lounsbury, Epstein, and Thode[b]	Nier[c]	Dibeler, Mohler, and Reese[d]
78	0.353 ±0.001	0.354 ±0.002	0.34	0.34	0.36
80	2.29 ±0.01	2.27 ±0.01	2.23	2.26	2.25
82	11.58 ±0.01	11.56 ±0.02	11.50	11.50	11.57
83	11.51 ±0.02	11.55 ±0.02	11.48	11.50	11.44
84	56.95 ±0.04	56.90 ±0.10	57.02	56.95	57.14
86	17.31 ±0.03	17.37 ±0.02	17.43	17.41	17.24

[a] See reference 3.
[b] Lounsbury, Epstein, and Thode, Phys. Rev. **72**, 517 (1947).
[c] A. O. Nier, Phys. Rev. **52**, 933 (1937) and private communication to H. G. Thode (see reference 5).
[d] Dibeler, Mohler, and Reese, J. Research Nat. Bur. Stand. **38**, 617 (1947).

precision of the measurements to Nier's most recent data. The agreement shows that it is possible to measure directly isotope abundances free from voltage discrimination errors by the use of magnetic scanning. This conclusion is of importance for measurements of abundances when a calibration mixture is not available.

[1] N. D. Coggeshall, J. Chem. Phys. **12**, 19 (1944).
[2] C. E. Berry, Phys. Rev. **78**, 597 (1950).
[3] A. O. Nier, Phys. Rev. **77**, 789 (1950); **79**, 450 (1950).
[4] O. A. Schaeffer and J. M. Hastings, J. Chem. Phys. **18**, 1048 (1950).

An Aid in Making Vibrational Assignments

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September 13, 1950

GENERALLY the only observed frequencies (obtained from Raman and infra-red spectra) which can be assigned unambiguously are those belonging to the totally symmetrical type. The depolarization data makes this possible. As a result, for a molecule of rather high symmetry there remain several more symmetry types to which assignments can be made with difficulty from considerations of the spectra only. Usually, calculations of the frequencies are made from a quadratic potential energy function.[1] The calculated frequencies are used then as a guide in assigning the observed frequencies to their respective types. Since the force constants employed to calculate the frequencies have been obtained from the simple potential function (i.e., no cross terms) for the totally symmetrical type, the calculated frequencies for the other type are at best only a first approximation.

Although the numerical agreement between observed and calculated frequencies under these conditions cannot be expected to be good, there is a definite relation between them which is of use in making the vibrational assignment. When there are n

modes in a symmetry type, this relation is of the form

$$\sum_{i=1}^{n} \frac{\Delta \lambda_i}{\lambda_i} \approx 0, \tag{1}$$

where $\lambda = 4\pi^2 c^2 \nu^2$ with ν in cm^{-1}.

From the relation[2]

$$\pi = GF, \tag{2}$$

in which

$\pi = \lambda_1 \lambda_2 \lambda_3 \lambda_4 \cdots \lambda_n$
$G = G$ matrix which is a function of masses only
$F = F$ matrix which is a function of force constants only

we see that

$$\frac{d\pi}{\pi} = \frac{dG}{G} + \frac{dF}{F}$$

$$= \frac{dF}{F} \text{ for no mass changes and no changes in geometry.} \tag{3}$$

For the case outlined above in which the F matrix is a function of the principal force constants only, viz. $F = K_1 K_2 K_3 \cdots K_n$, it is readily seen that

$$\frac{d\pi}{\pi} = \sum_{i=1}^{n} \frac{d\lambda_i}{\lambda_i} = \sum_{i=1}^{n} \frac{dK_i}{K_i}. \tag{4}$$

For the small changes in the force constants introduced when a set of force constants from one symmetry type is used to calculate the frequencies of some other type it can be shown[3] that

$$d\pi = 0 \tag{5}$$

and for larger differences that

$$\Delta \pi \approx 0. \tag{6}$$

Thus (1) follows from (6) and (4).

For a symmetry type containing two modes the relation gives

$$\frac{\Delta \lambda_1}{\lambda_1} \approx -\frac{\Delta \lambda_2}{\lambda_2},$$

i.e., the percent increase between the observed and calculated frequencies of one of the modes is nearly equal to the percent decrease for the other mode.

For the case where the symmetry type contains three modes, if the observed and calculated frequencies of one of the modes are quite close, i.e., $\Delta \lambda \approx 0$, the general expression will reduce to the two-mode case as a first approximation.

This criterion has already been used to advantage in assigning the 35 observed Raman and infra-red bands of the S_8 molecule.[1]

[1] H. J. Bernstein and J. Powling, J. Chem. Phys. **18**, 1018 (1950).
[2] E. B. Wilson, Jr., J. Chem. Phys. **7**, 1047 (1939); **9**, 76 (1941).
[3] This result and others concerned with "the change of frequency accompanying changes in mass, geometry, and force constants of a molecule" are considered in a paper which will appear in the *Canadian Journal of Chemistry* (1951).

Errata: Vibrational Intensities.
I. Theory of Diatomic Infra-Red Bands
[J. Chem. Phys. 18, 983 (1950)]

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AN error in our paper has been pointed out by Professor J. C. Decius which necessitates revision of certain of the relations given. In our Eq. (7), we omitted re-emitted radiation on the grounds that it would be isotropic. Actually, this is true only for spontaneous emission; induced emission is in the direction of the inducing radiation.[1] Consequently the term for induced emission should be included, as in our Eq. (7'); this leads to small changes in the subsequent equations.

Fundamentally, we must start from Eq. (7') instead of Eq. (7). We can regard this as a formal change which replaces $\omega_{v,i}{}^{v',i'}$ by

$\omega_{v,i}{}^{v',i'}[1-\exp(-hc\omega_{v,i}{}^{v',i'}/kT)]$ in Eqs. (10), (25), and (28). The last of these, written out correctly for evaluation, is now

$$A_v{}^{v'}=(8\pi^3 N_v/3hcZ)[\Sigma_{i,i'}\,\omega_{v,i}{}^{v',i'}\exp(-E_i/kT)S_{v,i}{}^{v',i'}$$
$$-\exp(-hc\omega_v{}^{v'}/kT)\Sigma_{i,i'}\,\omega_{v,i}{}^{v}{}_{,i'}$$
$$\times\exp(-E_{i'}/kT)S_{v,i}{}^{v',i'}].\quad(28')$$

The first sum, correctly evaluated in the original paper, led to Eq. (37). The evaluation of the second sum may be avoided by noticing that it is just like the first save for the appearance of $E_{i'}$ in the exponential instead of E_i. If we interchange j and j', the exponential is reduced to the former case; the line strength $S_j{}^{i'}$ is invariant; and we need only examine the effect on $\omega_{v,j}{}^{v',i'}$. This is given in Eq. (31), in terms of the parameter M; it is easy to see that interchange of j and j', which amounts to interchanging the R and P branches, changes the sign of M. Hence the interchange of j and j' reduces the second sum to the first sum, save for a change of sign of the term in $\bar{B}$, and of course multiplication by the vibrational Boltzmann factor.

So we may include these effects by writing Eq. (37) as

$$A_v{}^{v'}=(8\pi^3 N_v/3hc)\bar{\omega}_v{}^{v'}S_v{}^{v'},\quad(37')$$

where, however, Eq. (46) is revised to read

$$\bar{\omega}_v{}^{v'}=[\omega_v{}^{v'}+(B_{v'}-B_v)(1+Z)][1-\exp(-hc\omega_v{}^{v'}/kT)]$$
$$+2\bar{B}[1+\exp(-hc\omega_v{}^{v'}/kT)].\quad(46')$$

The summation to get the $A^{(n)}$ goes through as before, with the revised definition of $\bar{\omega}_v{}^{v'}$. The parameter Y_n, defined in Eq. (54), becomes

$$Y_n=[nx_e\omega_e(1-e^{-n\beta})+\alpha_e(1+e^{-n\beta})]/\bar{\omega}_0{}^n;\quad(54A)$$

with this change Eq. (54) through (57) are correct. Equation (58) is now better written as

$$A_0{}^n=(8\pi^3 N/3hcQ)(\mathbf{p}_0{}^n)^2\bar{\omega}_0{}^n.\quad(58')$$

Here $\bar{\omega}_0{}^n$ is a special case of $\bar{\omega}_v{}^{v'}$:

$$\bar{\omega}_0{}^n=[\omega_0{}^n+(B_n-B_0)(1+Z)](1-e^{-n\beta})+2\bar{B}_0{}^n(1+e^{-n\beta}).\quad(58A)$$

We are grateful to Professor Decius for calling this error to our attention.

[1] W. Heitler, *Quantum Theory of Radiation* (Oxford University Press, London, 1936), pp. 102 ff.

Electrolysis of Aluminum Solutions in a Magnetic Field

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THE formation of a molten mass-like deposit on the aluminum anode of an electrolytic cell with a platinum cathode and an electrolyte of unspecified concentration consisting of aqueous aluminum sulfate, in the presence of a magnetic field of 2000 gauss has been reported by Antonoff and Rowley.[1] These experiments have been repeated with magnetic inductions up to a maximum of 8160 gauss produced by an electromagnet with pole faces 1.19 cm in diameter and a gap of 7.1 mm. In most of the experiments pure metallic aluminum sheet was used as the anode material and a platinum wire or strip served as the cathode. Direct potential differences of from 5 to 40 volts were supplied by batteries and applied directly to the cell terminals. The total current in the various experiments was in the range of 0.0016 to 2.00 amp. The longest run at maximum magnetic field was 18 minutes in duration. Concentration of the aluminum sulfate solution ranged from 12.5 to 200 grams of $Al_2(SO_4)_3\cdot18H_2O$ per 100 cc of water. Temperature varied from 26 to 73°C and usually increased steadily during a particular experiment. In some of the experiments, the aluminum strip running from the anode proper to the cell terminal was in contact with the electrolyte; in others, it was insulated with paraffin wax. In one series of runs, Alcoa

type 24ST aluminum alloy was used as anode,[2] and in some instances the anode was scored in hopes that the scratches would serve as centers for formation of the deposit.[2] In a few runs, aluminum was used as anode and cathode.

In none of these experiments was a molten mass-like deposit formed on the anode. Corrosion of the anode was evident in all cases and tended to be somewhat more pronounced with the magnetic field. In one instance the pits resembled a crater, but with peaks and indentations reversed. Close inspection showed traces of an unidentified black deposit in the pits, possibly cupric oxide from small amounts of copper impurities.[3] There appeared to be no significant difference in results with and without the magnetic field. With the field, the solution became agitated by the charged gas bubbles, which rotated in spiral orbits. The motion of the liquid tended to remove the polarization gas bubbles and may account for the slight differences observed with and without the field.

If a significant magnetic effect exists under the conditions of the experiments described here, it is certainly difficult to reproduce. If such an effect does exist, one might expect the electromotive force of the cell to depend on the magnetic field. Palumbo and Riccobono[4] found only a slight effect on the emf which could be explained by considerations of thermal effects alone.

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[1] G. Antonoff and A. Rowley, Acta Physica Austriaca 2 (No. 1), 101–3 (1948); J. Phys. Colloid Chem. 52, 1105–8 (1948).
[2] Following suggestions of G. Antonoff, personal communication.
[3] W. E. Holland, Trans. Am. Electrochem. Soc. 53, 198 (1928).
[4] D. Palumbo and G. Riccobono, Ric. Scient. 18, 821–3 (1948).

Erratum:
Thermal Diffusion in the Critical Region. II

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IN Table I, page 1028, the heading of the fourth column should be " $\dfrac{\rho}{g/cc}$ "; the heading of the fifth column should be "$\Delta T°C$".

Also, the values of α' and α corresponding to separation factor of greater than one should be positive; i.e., the values of α' and α for runs 9, 10, 11, 26, 27, 28, 43L, 45, 46, 54L, 55L, 56L, 57L, 73L, 74L, 75L, 76L, 80, 81, 82, 89, 90, 91, 92, 93, 94 should have a positive sign.

Perturbations in the BaO Spectrum

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THE band spectrum of barium oxide—$^1\Sigma-^1\Sigma$-system investigated from about λ 5200 to 7000A—contains many perturbations.[1] All the perturbations are found in the upper levels and have been studied for $v'=1, 2, \cdots 5$; no perturbations have been found in $v'=0$. They can be explained as the results of interactions with four perturbing states called X, Y, Z, and Q. Most of the perturbations contain extra lines. The knowledge of the extra lines makes it possible to study the nature of the perturbing states.

A $^1\Sigma^+$-state—for BaO the states are with great probability $^1\Sigma^+$-states—can be perturbed not only by $^1\Sigma^+$ and $^1\Pi$-states but also by $^3\Pi$, $^3\Sigma^+$, and $^3\Sigma^-$-states. The ground states of the atoms, Ba(^1S) and O(^3P), give rise to a $^3\Sigma^-$ and a $^3\Pi$-state. We therefore consider that the states must be found among $^1\Sigma^+$, $^1\Pi$, $^3\Pi$, or