MASS ASYMMETRY EFFECT IN HUTCHISSON'S THEORY OF VIBRATIONAL TRANSITION PROBABILITIES

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· ABSTRACT:. Even though Hutchisson's theory of vibrational transition probabilities in diatomic molecules assumed the symmetry of constituent atomic masses, it was generally considered valid for asymmetric molecules too. Attempt has been made to examine this validity for some highly asymmetric molecules. It is concluded from the study of some band systems of BO, AlO, TiO and VO that considerable departures from theory result with increase in mass asymmetry.

Hutchisson (1930), while deriving his analytical expression for intensity of a band in an electronic transition, has made three important assumptions: (a) mechanical harmonicity, (b) mass symmetry and (c) electrical harmonicity (i.e. invariation of the electrical moment with γ, the internuclear distance). All these assumptions are not expected to actually prevail in practice. Leaving apart two of these assumptions, viz. mechanical harmonicity and electrical harmonicity we can investigate whether the third assumption, i.e. the nuclear mass symmetry of a molecule plays any significant part. It has been assumed by many that vibrational transition probability does not vary appreciably with disparity in the nuclear masses. In fact, the theory has been shown by Dunham (1930) to be applicable to asymmetric molecules too. The theory has actually been examined in asymmetric molecule BO by Elliott (1933) and in CN by McKellar and Buscombe (1948). The want of agreement, if any, has so far been usually attributed to anharmonicity of nuclear oscillations, which is not taken into account by theory. In view of the fact that disparities may be due to any or all of these three causes given above, it was thought desirable to examine molecules with predominant asymmetry in their atomic masses and the same varying by large margin from molecule to molecule, so that the effects, if any, due to other two factors may remain comparatively negligible. The asymmetry is expressed here as ρ, the ratio

of the heavier to the lighter atomic mass in the mlecule. The molecules chosen for this investigation are listed below with their mass asymmetry ρ :

Molecule :	$B^{11}O^{16}$	$Al^{27}O^{16}$	$Ti^{48}O^{16}$	$V^{51}O^{16}$
Mass asymmetry : (ρ)	1.45	1.7	3.0	3.2

One of the atomic masses, i.e. oxygen in the above series of molecules, is a constant and the other varies from B^{11} to V^{51}, giving a range of variability of ρ from 1.45 to 3.2. Thus, if asymmetry has any effect, it can very well be seen by the observed change of transition probability from molecule to molecule. The isotopic molecules are not chosen as they do not give a large range of variability in ρ and hence they are not considered to be of much consequence for the purpose of this problem.

The theoretical computations of transition probabilities are available in the case of one of these molecules, i.e. BO, through the work of Elliott (1933). In three others, the theoretical computations have been actually carried out in this work for the available 22 bands of AlO $^2\Sigma-^2\Sigma$, 23 bands of TiO $^3\Pi-^3\Pi$ and 19 bands of VO $^2\Delta-^2\Delta$ systems.

The experimental values of transition probabilities are already available for AlO and BO from the work of Tawde and Husain (1949) and Tawde and Trivedi (1939) and in the case of BO from the work of Elliott (1933). For the other systems, viz. TiO and VO, accurate determinations of intensity distributions have been made in the present work.

EXPERIMENTAL

The molecules TiO and VO were excited in carbon arc in air at atmospheric pressure. The source for TiO was titanium oxide in the powder form, which was packed in lower positive carbon electrode having 6 mm. diameter. The arc was fed from 230 volts D.C. mains with a suitable series resistance to obtain the desired current. Similar arrangement was made for exciting VO bands from the substance vanadic oxide. As the systems of TiO and VO chosen for study lie mostly in visible region, a Hilger glass prism spectrograph with a dispersion of 11 A.U. at 4200λ and 44 A.U. at 6000λ was employed.

The technique of photographic photometry was followed for quantitative estimation of intensities, which are taken as peak values near the band heads. This technique has been elaborated sufficiently in earlier papers particularly of Johnson and Tawde (1932), Tawde and Desai (1937) and Tawde and Patankar (1940). These values have been utilized to arrive at the estimation of experimental transition probabilities as the ratio $(I/\nu^4)v'v''/\sum\limits_{v'} I/\nu^4$ which could be very easily deduced from the measured values of I for each band.

The study of various aspects of intensity distributions other than the asym-metry effect in the band systems, are being reported elsewhere. For the relevance of the present problem, it was necessary to have only the comparison of the re-sulting values of experimental transition probabilities with the theoretical deri-vations from the analytical method of Hutchisson, employing harmonic oscil-lator. This theoretical derivation is indicated briefly in the following section.

THEORETICAL

According to Hutchisson (1930) the square of the following expression $P_{v'v''}$ gives the transition probability between vibrational levels v' and v'' :

$$P_{v'v''} = C_3 \frac{(v'!v''!)^{\frac{1}{2}}}{2^{(v'+v'')/2}} \sum_{l=0}^{v' \text{ or } v''} \sum_{i=0}^{(v'-l-1)/'} \sum_{j=0}^{(v''-l-1)'} a_{2l}b_{2i}c_{2j}d_{v'-2i-l} \, e_{v''-2j-l},$$

where C_3, a, b, c, d, e are expressible in terms of the quantities α and δ such that

$$\alpha = (\omega_0''/\omega_0')^{\frac{1}{2}}$$

$$\delta = 2\pi(\omega_0''\mu)^{\frac{1}{2}}(r_0'-r_0'')/h^{\frac{1}{2}}$$

involving the known constants ω_0, ω_0'', r_0, r'' and μ of the molecule.

From the above expression with the knowledge of various available constants (Herzberg, 1950) for the band systems of AlO, TiO and VO used here, the transition probabilities have been calculated. Such calculations on the β bands of BO are utilised from the earlier work of Elliott (1933).

RESULTS AND CONCLUSIONS

Table 1 below gives the calculated theoretical values of bands for the systems studied under the column marked T in each case. The corresponding ex-perimental value is entered side by side in column marked E.

By comparison of the two sets of values in Table I above, the number of bands showing approximately closer agreement for the molecules has been arrived at and the agreement is expressed on percentage basis as the ratio of this number to the total number of excitable bands of the system multiplied by 100. The results of this percentage agreement as a function of mass asymmetry are recorded in Table II.

It would be seen from Table II that the degree of agreement between theory and experiment is a function, among others, of the closeness in the two nuclear mass, i.e. mass symmetry. The closer the masses are, the better the agreement. The agreement is expected to deteriorate at higher quanta and

TABLE I

v', v''	$B^{11}O^{16}$		$Al^{27}O^{16}$		$Ti^{48}O^{16}$		$V^{51}O^{16}$	
	T	E	T	E	T	E	T	E
0, 0	0.20	0.24	0.73	0.51	0.45	0.42	0.11	0.35
0, 1	0.37	0.25	0.26	0.24	0.44	0.19	0.27	0.36
0, 2	0.28	0.30	0.03	0.10	0.22	0.13	0.67	0.45
0, 3	0.10	0.17	0.00	0.15	0.06	0.20	0.98	0.48
0, 4	—	—	—	—	0.01	—	0.48	0.20
0, 5	-	—	—	—	—	—	0.43	—
1, 0	0.25	0.25	0.22	0.28	0.37	0.37	0.34	0.41
1, 1	0.10	0.06	0.33	0.21	0.00_1	0.06	0.43	0.06
1, 2	0.06	—	0.40	0.22	0.38	0.11	0.32	0.14
1, 3	p.29	0.16	0.09	0.16	0.51	0.36	0.02	0.51
1, 4	—	—	0.01	0.10	0.18	0.21	0.10	0.31
1, 5	—	—	—	—	0.04	—	0.50	0.61
2, 0	0.21	0.29	0.05	0.21	0.19	0.21	0.56	0.23
2, 1	0.006	—	0.30	0.32	0.18	0.10	0.26	0.17
2, 2	0.14	0.13	0.12	0.12	—	—	0.00_1	0.40
2, 3	0.006	—	0.46	0.21	0.17	0.24	—	—
2, 4	—	—	0.18	0.17	0.55	0.33	0.26	0.24
2, 5	—	—	—	—	0.42	0.59	0.07	0.39
3, 0	0.14	0.13	—	—	—	—	—	—
3, 1	0.07	0.21	0.11	0.22	0.23	0.21	0.04	0.41
3, 2	0.05	0.05	0.28	0.35	--	—	—	—
3, 3	0.06	0.04	-	--	0.25	0.20	—	—
3, 4	—	-	0.51	0.25	--	—	—	—
3, 5	—	—	—	- -	0.55	0.40	—	—
4, 0	0.08	0.08	- -	--	—	- -	—	—
4, 1	0.56	0.22	—	—	0.15	0.43	—	—
4, 2	0.00	0.02	0.16	0.20	0.19	0.26	—	—
4, 3	0.09	0.20	0.24	0.37	-	—	—	—
4, 4	—	—	- -	—	0.26	0.45	0.16	0.25
5, 1	0.12	0.15	—	—	—	—	—	—
5, 2	0.03	0.18	- -	—	0.21	0.50	—	—
5, 3	0.01	—	0.21	0.16	—	—	—	—
5, 4	—	—	0.18	0.32	—	—	—	—
6, 4	—	--	0.12	0.17	—	—	—	—

N.B.—Pairs of values under T and E considered approximately close are entered in italics.

TABLE II

Molecule	Mass asymmetry ρ	Number of bands in approximate agreement	% of agreement
$B^{11}O^{16}$	1.45	12 in 19	63
$Al^{27}O^{16}$	1.7	9 in 22	41
$Ti^{48}O^{16}$	3.0	7 in 21	33
$V^{51}O^{16}$	3.2	3 in 18	17

with electrical anharmonicity in each case. These two factors, however, are not expected to change the measure of agreement by such a wide margin from molecule to molecule as obtained . Hence the effect seen here seems to be predominantly due to mass disparity between the two atoms, forming the molecule. It is thus obvious from the results of these experiments that in any application of Hutchisson's theory to diatomic molecules, effect of large mass asymmetry of the constituent atoms would have to be taken account of. The implied assumption of some that, it should be as much applicable to asymmetric molecules as to symmetric ones, has thus its limitations to the extent indicated above.

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REFERENCES

Dunham, J. L., 1930, *Phys. Rev.* **36**, 1553.

Elliott, A., 1933, *Proc. Phys. Soc.* **45**, 627.

Herzberg, G., 1950, Molecular Spectra and Molecular Structure—2nd Edn. D. Van Nostrand Co., New York.

Hutchisson, E., 1930, *Phys. Rev.* **36**, 410.

Johnson, R. C. and Tawde N. R., 1932, *Proc. Roy. Soc.* **A137**, 575.

McKellar, A., and Buscombe, W., 1948, *Pub. Dom. A. P. Ob.* **7**, 361.

Tawde, N. R., and Desai, D. D., 1937, *Proc. Ind. Acad. Sc.* **6**, 266.

Tawde, N. R., and Husain, A. G., 1949, *Bom. Univ. J*, **17**, 12.

Tawde, N. R. , and Patankar, V. S. 1940, *Bom. Univ. J.* **9**, 16.

Tawde, N. R. and Trivedi, S. A., 1939. *Proc, Phys. Soc* .**51**, 733.