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Relationship between torsional frequency and potential barrier height for AB_n type molecular system

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Abstract. A relationship between the torsional frequency (ν_{10}) and the potential barrier (V_n) has been determined for AB_n type molecular system having n-fold symmetry axis. It is found that ν_{10} varies prominently as $V_n^{1/2}$, V_n and V_n^2 in certain ranges. The V_n value computed from ν_{10} and I_r^* has been compared with that obtained from other experimental data for some AB_n units in different molecular-crystalline systems. Although there is in general a good agreement, in some cases the values differ significantly, perhaps due to the erroneous assignment of torsional mode and/or the large errors in the V_n value obtained from other experimental data.

Keywords. Torsional frequency; barrier height; potential barrier.

1. Introduction

The physico-chemical properties of a solid/large-molecule are considerably affected by the external rotatory modes of their small polyatomic groups. This happens because such modes have relatively low frequencies compared to the internal modes of the group. The study of these modes (particularly in relation to the symmetry and barrier height of the potential governing such motion) has been a subject of wide interest. For example, Gutowsky *et al* (1954) deduced the following relation between V_4 (the barrier height for the torsional motion around four-fold axis of a AB_4 type tetrahedral group in CsCl type lattice) and ν_{10} (the frequency of torsional mode of AB_4 about the same axis),

$$V_4 = \frac{1}{16}\left[h\,\nu_{10} + \frac{5\hbar^2}{2I}\right]^2 / (\hbar^2/2I), \tag{1}$$

where h is the Planck's constant and I (gm.cm^2) is the moment of inertia of AB_4 about its four-fold axis. Fateley and Miller (1961) and Venkataraman *et al* (1966) have discussed the utility of the well-known Mathieu's parameters (b and S as defined in the following section) in determining the torsional barrier respectively for XY_3 and AB_4 type rotors from the spectroscopically observed torsional frequency. The same approach has been discussed in detail by Durig *et al* (1972). Although these approaches are not complicated, the explicit nature of the relationship between the barrier height and the torsional frequency does not come to light. In this paper we discuss a semiempirical approach to find this relationship between ν_{10} and barrier height V_n in a potential of n-fold symmetry.

2. Theory

To a good approximation, the torsional mode of a restricted rotor of n-fold symmetry is governed by the potential (V) of the form (Venkataraman *et al* 1966)

$$V = \tfrac{1}{2} V_n (1 - \cos n\theta). \tag{2}$$

The Schrödinger equation for the problem with this potential takes the form of the well-known Mathieu's equation, *i.e.*

$$\frac{\partial^2 \psi}{\partial a^2} + (b - S \cos^2 a)\psi = 0, \tag{3}$$

with $2a = n\theta + \pi$. Here b and S, the two-dimensionless quantities known as Mathieu's parameters, are defined as

$$b = \frac{8\pi^2 I_r}{h^2} \cdot \frac{4}{n^2} \cdot E = F \cdot \frac{4}{n^2} \cdot E, \tag{4}$$

$$S = \frac{8\pi^2 I_r}{h^2} \cdot \frac{4}{n^2} \cdot V_n = F \cdot \frac{4}{n^2} \cdot V_n, \tag{5}$$

where E represents the energy of the rotor in its torsional state and $F = 8\pi^2 I_r / h^2$ stands for the reciprocal of the rotational constant; I_r is the reduced moment of inertia for internal rotation and is given by (Fateley and Miller 1961)

$$I_r = I_n \left\{ 1 - I_n \cdot \sum_k \frac{\lambda_k^2}{I_k} \right\} \tag{6}$$

Here I_n is the moment of inertia of the group about its symmetry axis, λ_k is the direction cosine of the angle between the axis of the internal top and the kth principal axis of inertia of the entire molecule. I_k is the principal moment of inertia of the entire molecule about kth principal axis.

Experiments like IR absorption and Raman scattering, etc. can in principle provide the energy difference $E = hc\nu_{mn}$ (c is the velocity of light and ν_{mn} is the frequency in cm^{-1}) between mth and the nth levels of the oscillating molecule. However, the fundamental frequency ν_{10} of an oscillating mode is in general found to be of greater interest. If this is not observed directly in any kind of spectrum of the sample, it can be easily deduced to a good accuracy from its overtones and combinations. Frequency ν_{10} can be related to the separation Δb_{10} ($= be_1 - be_0$) between two lowermost b-levels designated as be_1 and be_0 in tables relating to Mathieu's functions (Anon 1967) through

$$\Delta b_{10} = be_1 - be_0 = \frac{8\pi^2 I_r}{h^2} \cdot \frac{4}{n^2} \cdot hc\, \nu_{10}. \tag{7}$$

We therefore confine our efforts to study the variation of Δb_{10} with S in order to relate ν_{10} directly with V_n. The variation of Δb_{10} *vs* S is diagrammatically represented in figure 1. Standard values of be_1, be_0 and S from Anon (1967) have been used to plot the curve shown in this figure. Using the curve-fitting technique to find the suitable form of relation between Δb_{10} and S, we infer that:

(i) The S *vs* Δb_{10} curve closely resembles with a parabola having axis parallel to S-axis in $S \geqslant 2\,\Delta b_{10}$ region. This reveals that S varies dominantly as $\Delta b^2{}_{10}$ in this region and implies that ν_{10} varies dominantly as $(V_n)^{1/2}$ when $V_n \gg 2\nu_{10}$. This nature becomes more and more prominent as V_n increases much beyond $2\nu_{10}$ which indicates that the oscillation tends to become simple harmonic with the increase of barrier height.

(ii) In $S \leqslant \Delta b_{10}$ region, the S *vs* Δb_{10} curve closely resembles with a parabola having axis parallel to Δb_{10}-axis, which reveals that S varies dominantly as $(\Delta b_{10})^{1/2}$ in this region. It implies that ν_{10} varies dominantly as V_n^2 when $V_n \leqslant \nu_{10}$.

(iii) The point $S = 7{\cdot}0$ and $\Delta b_{10} = 3{\cdot}5$, on S *vs* Δb_{10} curve (figure 1), corresponds to $S = 2\Delta b_{10}$ and divides the curve into two parts consistent with the above mentioned observations. However, in a narrow region ($2{\cdot}5 \leqslant \Delta b_{10} \leqslant 4{\cdot}5$), which may be called as a region of transition from one kind of dependence to another kind, the dependence of S on Δb_{10} is linear.

(iv) Within error levels below 1·0%, S can be expressed in terms of Δb_{10} by

$$S = 0{\cdot}25\ (\Delta b_{10} + \beta)^2 \text{ when } \Delta b_{10} \geqslant 4{\cdot}5, \tag{8a}$$

with $\beta = 1 + (14{\cdot}8/\Delta b_{10}^2)$,

$$S = 2{\cdot}538\ \Delta b_{10} - 1{\cdot}87 : \text{when } 4{\cdot}5 \geqslant \Delta b_{10} \geqslant 2{\cdot}5, \tag{8b}$$

$$S = 7{\cdot}692\ (\Delta b_{10}^{1/2} - 1{\cdot}0) : \text{when } 2{\cdot}5 \geqslant \Delta b_{10}. \tag{8c}$$

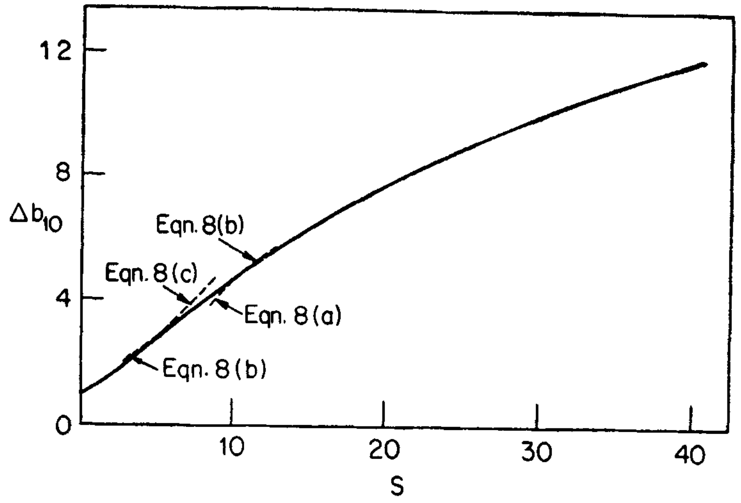


Figure 1. A curve showing the variation of standard values of $\Delta b_{10} = be_1 - be_0$ with those of S (values taken from Anon (1967)). The plot of equations 8(a), 8(b) and 8(c) in different regions as specified in the text coincide with the solid curve within the error levels below 1%; deviations of these plots from the solid curve are shown by dashed curves.

Using standard values of all universal constants equations (8a) to (8c) respectively take the following form suitable to calculate V_n (cal/mole) in a given problem,

$$V_n = 0{\cdot}102 \cdot \nu_{10}^2 \cdot I_r^* / n^2 + 1{\cdot}430 \cdot \nu_{10}\, \beta + 5{\cdot}002\, \beta^2\, n^2/I_r^*$$

$$\text{with } \beta = 1{\cdot}0 + 724 \cdot n^4/\nu_{10}^2\, I_r^{*2}, \tag{9a}$$

$$V_n = 7{\cdot}261\, \nu_{10} - 37{\cdot}013\, n^2/I_r^*, \tag{9b}$$

$$V_n = 58{\cdot}174\, n\, (\nu_{10}/I_r^*)^{1/2} - 153{\cdot}883\, n^2/I_r^*, \tag{9c}$$

where $I_r^* = I_r 10^{40}$. Out of the above relations, the one to be used for calculating V_n in a given problem, is decided by the range in which Δb_{10} falls. Δb_{10} can be easily determined through

$$\Delta b_{10} = 0{\cdot}143 \cdot \nu_{10}\, I_r^*/n^2, \tag{10}$$

which is obtained after putting standard values of all universal constants in (7); it does not require any data in addition to those needed for calculating V_n (*cf* equations (9a) to (9c)).

Equation (1) of Gutowsky *et al* (1954) can easily be simplified to:

$$V_4 = 0{\cdot}639 \times 10^{-2}\, I^*\, \nu_{10}^2 + 1{\cdot}787\, \nu_{10} + 125/I^*. \tag{11}$$

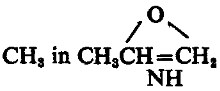
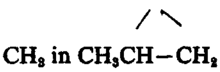
This is not different to a good approximation, from our relation (equation (9a)) which takes the following form for $n = 4$.

$$V_4 = 0.639 \times 10^{-2}\, I_r^*\, \nu_{10}^2 + 1{\cdot}430\, \beta\, \nu_{10} + 80{\cdot}0\, \beta^2/I_r^* \tag{12}$$

Note that β and β^2 lie respectively within 1·66 – 1·0 and 2·7 – 1·0 in the entire range of the applicability of (9a) and, therefore, (11) and (12) are almost the same. Thus it may be stated that Gutowsky's relation, though derived through a different procedure, is not different from (12) obtained from the results of Mathieu's equation.

In table 1, we summarise our calculated values of barrier height (V_n) for some typical molecular units in different molecular/crystal systems. These values are compared with values of V_n deduced from other experimental data such as microwave spectra, specific heat, spin-lattice relaxation time, etc. In general these two values agree well with each other. However, in some cases a significant difference is also observed. But this does not indicate any error in our relations [(9a)-(9c)] as our main relations (8a)-(8c), (which take the forms of (9a)-(9c) respectively) reproduce Δb *vs* S curve in their respective ranges with deviations below 1%; it may be mentioned that our calculated results resemble closely with those reported by others (*cf.* table 1). Further the V_n value obtained from experimental data such as microwave spectra, specific heat, etc., is deduced as the best fitting parameter needed to explain these results. The V_n value so deduced may sometimes have large errors. In fact equation (9) would provide the accurate value of V_n if the band due to torsional mode of AB_n measured at ν_{10} has been rightly picked up, since ν_{10} and V_n

Table 1. Barrier height for some typical molecular units.[a]

Unit	$I_r^* = I_r \cdot 10^{40}$ I_r (in g. cm^2)	ν_{10} (in cm^{-1})	V_n (Calculated)		V_n (Experimental) kcal/mole	Reference
			Ours kcal/mole	Others kcal/mole		
CH$_3$ in CH$_3$CH$_2$Cl	4·600	251·1	3·682	3·697	3·685 ± 0·011	1
CH$_3$ in CH$_3$CF=CH$_2$	4·981	191	2·360	2·367	2·441 ± 0·017	1
CH$_3$ in CH$_3$CH=CH$_2$	4·015	188	1·918	1·921	1·979 ± 0·017	1
 CH$_3$ in CH$_3$CH=CH$_2$	4·853	200	2·514	2·521	2·559 ± 0·071	1
 CH$_3$ in CH$_3$CH−CH$_2$	4·817	200	2·498	2·544	2·607 ± 0·025	2
NH$_4$ in NH$_4$Cl	4·826	390	5·285	5·400	5·298	3
NH$_4$ in NH$_4$Br	4·826	319	3·642	3·730	3·796	3
NH$_4$ in NH$_4$I	4·826	279	2·855	2·910	2·949	3
NH$_4$ in (NH$_4$)$_2$BeF$_4$	4·826	319(4)	3·642		3·156	4, 5
H$_2$O in Ba(ClO$_3$)$_2$H$_2$O	1·9187(6)	318(7)	5·006		5·0 (7)	6, 7
OH in C$_6$H$_5$OH	1·3118(8)	309·2(9)	3·664		3·402(8)	8, 9
BH$_4^-$ in NaBH$_4$	6·861(10)	240(10)	2·899		2·98 (10)	10
BH$_4^-$ in KBH$_4$	6·861(10)	244(10)	2·989		3·44 (10)	10

[a]values of I_r, ν_{10}, V_n (calculated as well as experimental) reported by others are from references given in column 7 and more specifically given in paranthesis.

1. Fateley and Miller (1961)
2. Durig *et al* (1972)
3. Gutowsky *et al* (1954)
4. Jain (1974)
5. O'Reilly *et al* (1967)
6. Eisenberg and Kauzmann (1969)
7. Ross (1972)
8. Quade (1968)
9. Bist *et al* (1967)
10. Smith (1974)

are directly related with each other. The accuracy of V_n would depend on the accuracy of ν_{10} and I_r. Thus the significant difference observed in the V_n value calculated through (9) and that obtained from other experimental data is an indication of errors in ν_{10} (*i.e.* the assignment of torsional mode could be wrong) and/or V_n obtained from other sources.

3. Conclusion

In conclusion, it may be mentioned that this study reveals some important aspects of the correlation found between the torsional frequency (ν_{10}) and the barrier height (V_n). It is hoped that the semi-empirical relations (equation (9a) to (9c)) should considerably simplify the process of evaluating V_n from ν_{10}, I_r^* and n. It may be suggested that a significant difference in the computed value of V_n (through (9)) and that obtained from other experimental data is an indication for an erroneous assignment of torsional mode and/or large errors in the latter value.

References

Bist H D, Brand J C D and Williams D R 1967 *J. Mol. Spectrosc.* **24** 402

Durig J R, Craven S M and Harris W C 1972 in *Vibrational spectra and structure* (ed) J R Durig, (New York: Marcel Dekker) Vol. 1, p. 73

Eisenberg D and Kauzmann W 1969 *The structure and properties of water* (Oxford: Clarendon Press) p. 4

Fateley W G and Miller F A 1961 *Spectrochim. Acta* **17** 857

Gutowsky H S, Pake G E and Bershon R 1954 *J. Chem. Phys.* **22** 643

Jain Y S 1974 *Spectra structure correlations in certain polyatomic systems* Ph.D. Thesis I.I.T. Kanpur (India) p. 160

Quade C R 1968 *J. Chem. Phys.* **48** 5490

O'Reilly D E, Peterson E M and Tsang T 1967 *Phys. Rev.* **160** 333

Ross S D 1972 *Inorganic infrared and Raman Spectra* (London: McGraw Hill) p. 133

Smith D 1974 *J. Chem. Phys.* **60** 958

Tables relating to Mathieu functions, Anon 1967 National Bureau of Standards, Applied Mathematics Series

Venkataraman G, Denis K Usha, Iyengar P K, Roy A P and Vijayaraghavan P R 1966 *J. Phys Chem. Solids* **27** 1103