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Improvement of the standard method for solving the problem of internal rotation in molecules with symmetrical tops

V. I. Tyulin, P. A. L. Batchy-Tom, and V. K. Matveev*

Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow, Russian Federation. Fax: +7 (095) 932 8846. E-mail: tyulin@conformer.chem.msu.su; batchy@phys.chem.msu.ru

Drawbacks of the standard method for solving the problem of internal rotation (IR) in molecules with symmetrical tops were examined. The drawbacks can be eliminated by taking into account the higher harmonics of the IR potentials. A new calculation procedure based on the approximation of the lower portion of the potential curve by the equation $V(\varphi) = 1/2\ V_n^*(1 - \cos n\ \varphi)$, which describes adequately the arrangement of the torsion levels, was proposed. The successfull implementation of the proposed procedure showed that the procedures used currently are incorrect as well as the Herschbach procedure, which includes a systematic error at each iteration step.

Key words: internal rotation, torsion frequency, vibrational spectra, microwave spectra; chloroethane; propylene; propylene oxide; phenol.

In the elementary case of internal rotation (IR), the potential function has the form

$$V(\varphi) = 1/2\ V_n(1 - \cos n\ \varphi), \qquad (1)$$

where n is the multiplicity of the function in the section from 0 to 2π, and φ is a dihedral angle of IR. This potential corresponds to rotation of one part of the molecule, called "top," in relation to another part, which is called "frame".[1] It has been shown[2] that if the properties of the symmetry of the top and the frame are specified by numbers σ_1 and σ_2, the multiplicity of the potential n is determined by the formula

$$n = (\sigma_1 \cdot \sigma_2)/M,$$

where M is the greatest common multiple for the numbers σ_1 and σ_2. Typical examples are presented in a previous publication.[2] This case of IR encompasses, in particular, a large group of molecules for which σ_1 (or σ_2) is equal to unity.

The direct IR problem includes finding the eigenvalues (energy levels) and the eigenvectors (wave functions) for the given potential (1). The kinetic factor is specified as

$$F = F_0 + \Sigma F_k \cos k\ \varphi,$$

where $F_0 = h\ /\ 8\pi^2 c I_r$.

In the rigid-top approximation, $F = F_0$; for such problems, by using the Hamiltonian of the form

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$$\hat{H} = -F_0 \frac{\partial^2 \psi}{\partial \varphi^2} + \frac{1}{2} V_n (1 - \cos n\varphi)\psi, \quad (2)$$

and by substituting (2) into the Schrödinger equation, we obtain the Mathieu equation

$$y''(x) + (b - S\cos^2 x)\, y = 0, \quad (3)$$

where $b = 4E/n^2F$; $S = 4V_n/n^2F$;

$$x = (n\varphi + \pi)/2; \; y = \psi(\varphi). \quad (4)$$

Then

$$\Delta E_{v,\sigma} = (n/2)^2 F \Delta b_{v,\sigma}, \quad (5)$$

$$V_n = (n/2)^2 FS. \quad (6)$$

Solution of Eq. (3) comprises tabulated eigenvalues $b = f(S)$. In a potential well of depth V_n, each value of the parameter S is matched by a definite number of $b_{v,\sigma}$ values, which depend on the vibrational quantum number v and the symmetry of the torsion level σ. The field of tabulated $b_{v,\sigma}$ for S, later, $\Delta b_{v,\sigma} = \Phi(S)$, was first (historically) calculated for small v and n (up to $n = 3$). Previously (see Ref. 1, p. 195), references for the Mathieu tables for different n, large S, and high v values have been reported; new methods for solution of the Mathieu equation for integer and noninteger n have been proposed.[3,4]

Equation (3) holds only for integer n; $\Delta E_{v,\sigma}$ corresponds to the experimental difference between two particular levels with specified n. The reverse problem is solved according to the scheme $\Delta E_{v,\sigma} \rightarrow \Delta b_{v,\sigma} \rightarrow S \rightarrow V_n$. For the simplest potential (1), the IR problem is considered to be solved at this stage. The main advantages of the standard method are simplicity of using experimental information and finding the solution itself. Note that, according to Eqs. (5) and (6), knowing F, n, and $\Delta E_{v,\sigma}$ even for one particular transition enables determination of S and V_3. The $\Delta E_{v,\sigma}$ value can be measured using various experimental methods, IR, Raman, and microwave spectra, *etc.*[1] The solution of the problem for acetaldehyde[6,7] and phenol[8,9] molecules can be cited as typical examples. The F_0 value was calculated from the geometric parameters of molecules or estimated directly from the rotational spectra. This provides satisfactory results for small molecules. Thus, the standard method for molecules with symmetrical tops allows fast and simple estimate of the V_n barriers with an accuracy of ~ 5%, which is the main advantage of this method. This procedure is widely used in microwave spectroscopy for the calculation of V_3 for the methyl groups contained in various organic molecules, because the rotation constants for these groups depend on the symmetry of torsion levels (A, E). It is possible to use this dependence and the A/E splitting value for estimating V_3 (see Ref. 1, p. 157).

However, the above-outlined method for the calculation of V_n is merely a first-approximation estimate. A real $V(\varphi)$ potential cannot be described by only one harmonic. In the general case, multiple harmonics should also be taken into account for the function $V(\varphi)$. Herschbach[5] was the first to develop a standard method for taking account of corrections $k = V_{2n}/V_n$, which has been repeatedly used in practice.[10] However, this method is very inconvenient. The procedure of refinement of potential (1) with the help of the correction $k = V_{2n}/V_n$ proved to be iterative, and the result obtained at each iteration step depended on the initial approximation and contained a systematic error. Attempts have been made[10–12] to analyze other complications of this method. The outcome of these efforts can briefly be formulated as follows. First, the standard method gives different V_3 values depending on the particular method used to calculate the parameter F. Second, the result was found to depend on the isotope substitution, *i.e.*, in some cases, the V_3 values for the CH_3 and CD_3 groups were different.[13] The discrepancy between the experimental and calculated frequencies remains large and sometimes exceeds experimental errors by an order of magnitude.[9] In addition, the procedure of refinement of the V_6/V_3 correction[5] is not very convenient because it requires numerous tentative calculations. Other possible errors have also been analyzed;[10] this led to the important conclusion that the major error is due to neglecting the V_6 value.

When calculating Δb from Eq. (5), one should take into account the numbers n and F, which always introduce errors. First, this is due to the fact that the F value depends on the available structural parameters of a molecule, which always contain inaccuracies, and, second, F depends on φ. However, the most significant error is due to the fact that n, which should be an integer according to the meaning of expression (1), is no longer an integer in Eqs. (4)—(6). In fact, let the real $V(\varphi)$ potential consist of the sum of only two harmonics

$$V(\varphi) = 1/2\, V_n(1 - \cos n\varphi) + 1/2\, V_{2n}(1 - \cos 2n\varphi). \quad (7)$$

Having calculated the second and fourth derivatives of this potential in the point $\varphi = 0$, we obtain

$$A = 2V^{(2)}(\varphi = 0) = n^2 V_n + 4n^2 V_{2n} = n^2 V_n (1 + 4k), \quad (8)$$

$$A \cdot B = 2V^{(4)}(\varphi = 0) = n^4 V_n + 16n^4 V_{2n} = n^4 V_n (1 + 16k), \quad (9)$$

where $k = V_{2n}/V_n$ is much less than unity. Having divided Eq. (9) by Eq. (8), we get

$$B = n^2 [(1 + 16k)/(1 + 4k)] = (n^*)^2.$$

Thus, the dependence of this ratio on the multiple harmonics V_{2n} "distorts" the B value, which should be equal to n^2 at $k = 0$. In reality, the ratio of these derivatives is no longer an integer squared, which can easily be taken into account. Let $n^* = n\gamma$, then

$$(n^*/n)^2 = \gamma = (1 + 16k)/(1 + 4k). \quad (10)$$

Thus, n appears in Eqs. (5) and (6) not as an integer but as an n^* value, which has a meaning of a calculable parameter, which differs from the symmetry parameter n. In real cases, $k \neq 0$ and, hence, $n^* \neq n$ and $\gamma \neq 1$. In the calculations according to the standard procedure, when it is necessary to find the $V(\varphi)$ potential in the more precise form (7), one should first calculate n^*. This could be done using experimental data and Eq. (5)

Table 1. Comparison of the torsion frequencies (ω_{exp} and ω_{calc}/cm^{-1}) for various molecules

Δv	σ	ω_{exp}[13]	ω_{calc}	$\Delta\omega$	$Db_{v,\sigma}$	N^*	V_3^*/cm^{-1}
			EtCl (S = 96.96)				
0—1	A	250.50	250.35	0.15	18.63487	2.2245	1303.4
0—1	E	250.50	251.35	0.15	18.63483	2.2245	1303.4
1—2	A	234.80	234.87	−0.07	17.48231	2.2225	1302.3
1—2	E	234.80	234.89	−0.09	17.48352	2.2224	1302.2
2—3	A	217.60	217.56	0.04	16.19356	2.2236	1302.9
2—3	E	(194.0)	217.89	−0.06	16.17142	2.2226	1302.3
3—4	A	(197.6)	194.16	−0.16	14.45182	2.2214	1301.6
3—4	E		197.53	0.07	14.70288	2.2240	1303.1
				±0.106*		2.2232*	1302.7(6)*
			CH_3CD_2Cl (S = 97.52)				
0—1	A	247.7	247.11	0.59	18.6914	2.2538	1292.4
0—1	E	247.7	247.11	0.59	18.69136	2.2538	1292.2
1—2	A	231.7	231.88	−0.18	17.53948	2.2466	1288.2
1—2	E	231.7	231.90	−0.20	17.54063	2.2465	1288.2
2—3	A	214.6	214.86	−0.26	16.25157	2.2457	1287.7
2—3	E	214.3	214.57	−0.27	16.23031	2.2455	1287.6
3—4	A	(191.9)	191.96	−0.06	14.51992	2.2477	
3—4	E	(195.1)	195.17	−0.07	14.76248	2.2476	
				±0.34*		2.2484*	1289(2)*
			Propene (S = 43.81)				
0—1	A	191	191.35	−0.35	12.4699	2.2428	688.9
0—1	E	191	191.22	−0.22	12.1387	2.2443	689.4
1—2	A	169.8	169.56	+0.24	10.76405	2.2500	691.2
1—2	E	171.8	171.84	+0.04	10.90845	2.2464	690.0
2—3	A	158.6	158.32	−0.28	10.05015	2.2509	691.4
2—3	E	—	137.88	—		—	—
				±0.27*		2.2469*	690(1)*
			2-Fluoropropene (S = 66.42)				
0—1	A	190.47	190.49	−0.02	15.22596	2.2243	830.9
0—1	E	190.47	190.48	−0.01	15.22527	2.2244	830.9
1—2	A	175.12	175.34	−0.22	14.01536	2.2217	829.9
1—2	E	175.12	175.55	−0.43	14.03204	2.2191	828.9
2—3	A	160.0	159.40	0.6	12.74103	2.2329	834.1
2—3	E	156.6	156.58	0.02	12.51541	2.2249	836.1
				±0.32*		2.2245*	831(2)*
			Propylene oxide (S = 74.03)				
0—1	A	200	200.09	−0.09	16.13865	2.18257	917.4
0—1	E	200	200.09	−0.09	16.13832	2.18261	917.4
1—2	A	185.8	185.34	0.46	14.94926	2.18892	920.1
1—2	E	185.8	185.45	0.35	14.95768	2.18769	919.6
2—3	A	168.8	169.21	−0.41	13.64825	2.17821	915.6
2—3	E	167.5	167.67	−0.17	13.52356	2.18137	916.9
				±0.3*		2.1836*	918±2*
			Thiopropene (S = 105)				
0—1	A	223.6	223.64	−0.04	19.43745	2.0469	1207.9
0—1	E	223.6	223.64	−0.04	19.43743	2.0469	1207.9
1—2	A	210.4	210.47	−0.07	18.29325	2.04653	1207.7
1—2	E	210.4	210.48	−0.08	18.29388	2.04646	1207.6
2—3	A	196	195.79	0.21	17.01718	2.04943	1209.4
2—3	E	—	195.65	—	17.00481		—
				±0.09*		2.1497*	1208(1)*

Note. The values in parentheses are inaccurate. * Average.

if S and $\Delta b_{v,\sigma}$ were known. This is possible only in the case where S can be found independently of n and F (see below). The calculations of n^* from experimental data for a series of particular molecules confirm that $n^* \neq n$ (Tables 1—2).

Let us consider first of all the calculations that makes it possible to find both parameters, V_n and V_{2n}, by a standard procedure provided that n^* is used instead of n. From Eq. (10), we obtain

$$k = 1/4(\gamma^2 - 1)/(4 - \gamma^2),$$

and Eq. (6) will be transformed into the new expression

$$V_n^* = (n^*/2)^2 FS = N^* FS. \qquad (11)$$

From Eq. (8), we have

$$A = n^2 V_n(1 + 4k) = (n^*)^2 V_n^*,$$

then

$$V_n = V_n^*(n^*/n)^2\ 1/(1 + 4k) = \\ = V_n^*\ (1 + 16k)/(1 + 4k)^2. \qquad (12)$$

Tables 1—2 present examples of calculation of Δb in terms of this scheme (see Eqs. 10 and 11); this is purposely done for those molecules that have been used in the literature to demonstrate the difficulty of the method.[8—12] We eliminated virtually all of the drawbacks mentioned above, and the agreement between experimental and calculated values for torsion frequencies now completely corresponds to the accuracy of the experiment. It should be specially noted that the parameters n^* prove to be identical for all transitions, except for the higher transitions, for example, $3 \rightarrow 4$, *etc.*, which are normally measured in the spectra less accurately, due to their low intensity.

It remains to be explained how one can calculate the S value without using n or F. The calculation of Δb from Eq. (5) does not give the correct answer, because we are compelled to use an integer n. However, by dividing Eq. (5) by (6), we obtain

$$\Delta E_{v,\sigma}/V_n = \Delta b_{v,\sigma}/S = \chi(S)$$

$$\text{or } V_n = S/\Delta b_{n,s} \cdot \Delta E_{n,s}. \qquad (13)$$

Table 2. Comparison of the torsion frequencies (ω_{exp} and ω_{calc}) of the phenol molecule and its derivatives

$\Delta\nu$	σ	ω_{exp}[13]	ω_{calc}	$\Delta\omega$	$\Delta b_{v,\sigma}$	N^*	V_2^*/cm^{-1}
			Phenol (S = 45.27)				
0—1	*A*	309.0	308.66	0.34	12.36641	1.1550	1131.3
0—1	*B*	308.8	308.43	0.37	12.35715	1.1550	1131.3
1—2	*A*	275.4	275.33	0.71	11.00546	1.1566	1132.8
1—2	*B*	279.3	279.20	0.40	11.17380	1.1553	1131.6
2—3	*A*	254.1	254.66	−0.7	10.20833	1.1505	1126.9
2—3	*B*	(217)	219.84	−0.77	8.72495	1.1495	—
				±0.58*		1.1549(1)*	1130(1)*
			para-d-Phenol (S = 43.75)				
0—1	*A*	308.9	308.9	0	12.4751	1.1447	1139.0
0—1	*B*	308.8	308.8	0.1	12.4666	1.1455	1139.4
1—2	*A*	276.9	275.5	1.4	11.1242	1.1435	1145.0
1—2	*B*	278.8	279.3	−0.5	11.2807	1.1354	1136.9
2—3	*A*	(251.1)	254.8	−3.7	10.2894	—	1122.6
2—3	*B*	(217.2)	219.9	—	8.8823	—	1124.8
				±0.5*		1.1423(46)*	1135(9)*
			para-F-Phenol (S = 42.58)				
0—1	*A*	279.1	279.1	0.1	12.1753	1.0690	1008.6
0—1	*B*	279.0	278.8	0.2	12.1645	1.0700	1009.2
1—2	*A*	247.1	247.4	−0.3	10.7953	1.0670	1007.1
1—2	*B*	—	251.8	—	10.9864	—	—
2—3	*A*	(219.6)	230.8	—	10.0701	—	—
2—3	*B*	(187.9)	193.5	—	8.4454	—	—
				±0.2*		1.0687*	1008*
			para-F-Phenol-*OD* (S = 84.37)				
0—1	*A*	211.4	211.6	−0.7	17.3064	1.0715	1028.4
0—1	*B*	211.3	211.5	0.16	17.3063	1.0710	1028.0
1—2	*A*	197.3	197.2	0.12	16.1370	1.0725	1029.7
1—2	*B*	197.4	197.3	0.17	16.1416	1.0727	1029.9
2—3	*A*	(181.2)	181.2	−0.04	14.8329	—	—
2—3	*B*	(180.3)	180.3	−0.02	14.7578	1.0717	—
				±0.11*		1.0718*	1030(9)*

Note. The values in parentheses are inaccurate. * Average values.

Thus, V_n can be immediately calculated if the S value is known, because $\Delta E_{v,\sigma}/V_n$ does not depend on F. Taking account of expression (13), this can be done without using the tabulated values $\Delta b = f(S)$ but by finding new functions, $\Delta b_{v,\sigma}/S = f(S)$ or $\Delta b_i/\Delta b_2 = \Phi(S)$, for the solutions of the Mathieu equation. Neither of these functions depends on F. This possibility is well realized in practice if the solutions of the Mathieu equation are employed as modified tables. We also attempted to find an analytical expressions for these functions. Analysis shows that it is not always possible. The difficulty is due to the fact that the relevant curves sometimes have several inflection points (*i.e.*, they have several roots) and are not monotonic. Nevertheless, for some transitions, the analytical expressions were retrieved; they can be used for choosing S as the first approximation.

Table 3. Calculation of S for the $MeCH_2Cl$ molecule

k	S_k	dS_k	dS/dX	$x =$ ω_i/ω_j	Transition i	Transition j
1	96.58	−0.38	−9.07	1.151	0-1*A*	2-3*A*
2	96.51	−0.45	−2.63	1.291	0-1*A*	3-4*A*
3	97.86	0.89	−16.96	1.079	1-2*A*	2-3*A*
4	96.77	−0.19	−3.26	1.210	1-2*A*	3-4*A*
5	96.48	−0.48	−4.49	1.122	2-3*A*	3-4*A*
6	96.19	−0.77	−8.16	1.153	0-1*E*	2-3*E*
7	96.84	−0.12	−4.43	1.268	0-1*E*	3-4*E*
8	97.11	0.14	−14.07	1.081	1-2*E*	2-3*E*
9	97.48	0.51	−6.12	1.188	1-2*E*	3-4*E*
10	97.82	0.85	−12.69	1.099	2-3*E*	3-4*E*
	96.96*	±0.55*				

* Average.

However, generally, it can be concluded that the accuracy of calculation of S from analytical dependences is usually not very high but suffices for restricting the area of the search for the required solution. It is clear that the S values must be identical for all the torsion frequencies and for all of their ratios. Hence, a more accurate S value can be determined by averaging several such ratios. The corresponding programs were composed according to which the S value is found as the average of several ratios between transitions by using the solutions of the Mathieu equation, available from previous publications.[3,4] In practice, this approach proved to be convenient for determination of S. The CH_3CH_2Cl molecule, for which the corresponding calculations for S are listed in Table 3, can serve as an example. The S values found for different isotope compositions of this molecule (see Table 1) are quite consistent with one another. Thus, in the presence of excess information, the calculation of S from the $\Delta E_i/\Delta E_j$ ratios for various experimental frequencies makes it possible to find S values that do not depend on F and are nearly equal for various levels. It is easy to verify that the V_3 and V_6 parameters for isotope-substituted sorts of the same molecule now coincide to within determination errors (see Table 4). Thus, we eliminated the difficulties that had previously been involved in the conventional use of the standard Mathieu tables. It is rather interesting to compare the potential of the new method and the Laane method.[14]

The meaning of the introduction of the parameter n^* lies in the fact that to attain a better description of the experimental levels, we introduce an effective potential with a different period, *i.e.*, we actually replace potential (7) near the main minimum by an effective potential with one harmonic $V_n^*(1 - \cos n^*\varphi)$, where n^* is a noninte-

Table 4. Calculated parameters and the V_n and V_{2n} values of the molecules studied

Molecule	F	S	n^*	K	V_n^*	V_n	V_{2n}	V_n	V_{2n}	Reference
CH_3CH_2Cl	6.043	96.96	2.982	−0.001	1303(6)	1292	−1.3	1291	0	10
								1289	0	13,18
CH_3CD_2Cl	5.88	97.52	2.9989	−0.0006	1289(3)	1288.6	−0.3	1289	0	13
								692	0	16
$CH_3CH{=}CH_2$	7.01	43.81	2.9979	−0.00012	690(1)	689.5	−0.1	693.7	−14	21
								711	16	10
								854	0	17
$CH_3CF{=}CH_2$	5.657	66.42	2.974	−0.0014	831(2)	821.4	−1.2	818	4	10
								895	0	12
CH_3CHOCH_2	5.678	74.03	2.9554	−0.0024	918(2)	899.5	−2.2	900	−9	10
CH_3CHSCH_3	5.620	105.0	2.8616	−0.0073	1208(1)	1132.2	−8.3	1140	0	10
C_6H_5OH	21.636	45.27	2.1481	0.0135	1130(3)	1236.8	16.7	1189	0	8,9
para-D-C_6H_4OH								1242.8	0	8
	21.68	43.75	2.1376	0.01245	1135(9)	1235	15.4	1188	0	9
para-F-C_6H_4OH	21.567	42.58	2.068	0.0059	1008(1)	1053	6.2	1007	0	9
para-F-C_6H_4OD(**10**)	11.40	84.37	2.071	0.0061	1031(1)	1078.5	6.6	1034	0	9

Note. The F, V_n, and V_{2n} values are expressed in cm^{-1}.

ger, by equalizing the second and fourth derivatives of both potential curves in this region. This technique also proved to be convenient for the calculation of thermodynamic functions for asymmetrical IR potentials.[20]

Thus, the standard procedure involving the use of integer n was faced with numerous contradictions, because real levels correspond to potential (7), *i.e.*, they include the terms V_{2n}, V_{3n}, *etc.* It was suggested that the parameter n in Eqs. (5) and (6) be regarded as noninteger. The calculation of n^* from experimental data confirmed this conclusion. Hence, the previously used methods including the procedure of taking account of the correction $k = V_{2n}/V_n$ [5] were inaccurate. It can be seen from Eq. (8) that V_6 and V_3 are dependent on each other and the correction $k = V_6/V_3$ cannot be used directly, because every new V_6 value distorts the corresponding V_3 value. This technique was to be applied repeatedly, and at each step errors were introduced. The outcome can be substantially improved by using n^* instead of n. In essence, the n^* value effectively takes into account the influence of higher harmonics. The calculation procedure does not involve any fundamental difficulties, and the results of calculations correspond more accurately to the experimental data.

Further improvement and perfection of this approach are associated with the search for a more accurate description of the $F(\varphi)$ dependence. This provides the possibility of refining the previously determined IR potentials for molecules with symmetrical tops. This is true not only for molecules with $n = 3$ (or 2) but also for those with $n = 4, 5, 6, 8, 12, \ldots$, in particular, ferrocene type molecules.[22] However, solution of problems of this type requires composing Mathieu tables for large n, new programs that would take into account more complex properties of the level symmetry, *etc.*

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