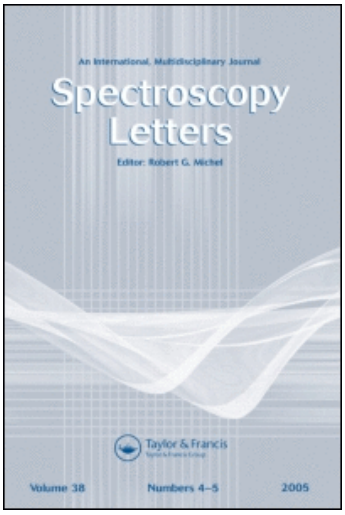

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Improved Determination of Barrier Heights from Self-consistent Harmonic Approximation

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IMPROVED DETERMINATION OF BARRIER HEIGHTS FROM SELF-CONSISTENT HARMONIC APPROXIMATION

Key Words: Torsional barrier heights

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In a preceding paper [1] we have given an explicit formula for calculating the barrier height V_3 for one-top molecules as a function of the experimental torsional frequency and of geometry (see formula 20). We point out, however, that the actual expression for V_3 is given in terms of the self-consistent harmonic torsional frequency ω^c as follows [1]:

$$V_3 = (\omega^{c\,2}/9F)\exp(9F/2\omega^c) \qquad (1)$$

Since the torsional frequencies $\omega_{o\to1}$ and $\omega_{o\to2}$ corrected to second order by using the self-consistent harmonic approximation are given by [2]:

$$\omega_{o\to1} = \omega^c - \frac{81F^2}{32\omega^c} \qquad (2)$$

$$\omega_{o\to2} = 2\omega_c - \frac{9F}{4} - \frac{1053}{64}\,\frac{F^2}{\omega_c} \qquad (3)$$

one can derive, with a very good approximation, ω^c as a function of geometry, $\omega_{o\to1}$ and $\omega_{o\to2}$ respectively:

$$\omega_1^{\,c} \simeq \omega_{o\to1} + \frac{81F^2}{32\omega_{o\to1}} \qquad (4)$$

$$\omega_2^c \simeq \frac{1}{2}\left(\omega_{o\to 2} + \frac{9F}{4}\right) + \frac{1053F^2}{64(\omega_{o\to 2} + 9F/4)} \qquad (5)$$

In Table 1 the values of $\omega_{o\to 1}$ and $\omega_{o\to 2}$ obtained from eqs. (2) and (3) and those from the solution of the Mathieu's equation are reported. The two sets of data show generally a very good agreement. For the last four medium barrier height molecules, the values of $\omega_{o\to 2}$ from eq. (3) shows a better agreement with the E→E transitions.

TABLE 1

Comparison between $\omega_{o\to 1}$ and $\omega_{o\to 2}$ from eqs. (2) and (3) and those from Mathieu's equation

Molecule	F^a	ω_c^a	eqs.(2-3)		Mathieu	
CH_3CH_2Cl	6.067	251.27	$\omega_{o\to 1}$	250.9		250.8
			$\omega_{o\to 2}$	486.48		485.9
CH_3CH_2Br	5.895	247.78		247.42		247.4
				479.99		479.5
CH_3CH_2I	5.770	228.88		228.51		228.4
				442.38		441.7
CH_3SiH_3	8.217	183.69		182.76	Av.	182.6
				342.84	A	332.6
					E	341.9
CH_3GeH_3	8.106	158.40		157.35	Av.	157.1
				291.74	A	275.7
					E	291.4
CF_3SiH_3	5.530	142.43		141.89	Av.	141.7
				268.88	A	265.2
					E	267.9
CH_3NH_2	15.488	273.21		270.99	Av.	270.6
				497.13	A	458.6
					E	498.2

(a) From ref. 1. All values are in cm^{-1}

TABLE 2

Comparison between the barrier heights evaluated from ω_1^c, ω_2^c and those from microwave

Molecule	F	$\omega^a_{o\to1}$	$\omega^a_{o\to2}$	ω_1^c	ω_2^c	$V_3(\omega_1^c)$	$V_3(\omega_2^c)$	V_3(MW)
CH_3CH_2Cl	6.067	250.8	485.9	251.17	250.99	1288	1286	1289
CH_3CH_2Br	5.895	247.4	479.5	247.75	247.54	1288	1286	1288
CH_3CH_2I	5.770	228.4	441.7	228.77	228.55	1129	1127	1130
CH_3SiH_3	8.217	Av 182.55	A 332.6 E 341.9	183.49	A 178.71 E 183.28	557	A 531 Av 543 E 556	558
CH_3GeH_3	8.106	Av 157.1	A 275.7 E 291.4	158.16	A 150.65 E 158.31	432	A 396 Av 414 E 433	433
CF_3SiH_3	5.530	Av 141.7	A 265.2 E 267.9	142.25	A 140.63 E 141.97	484	A 474 Av 478 E 483	485
CH_3NH_2	15.488	Av 270.6	A 458.6 E 498.2	272.84	A 254.72 E 273.93	690	A 612 Av 653 E 694	691

a From solution of Mathieu's eq.

We wish to show that the values of V_3 evaluated from eqs. (1) and (4) are in better agreement with the MW data than those obtained in ref. 1 where the crude approximation $\omega^c \simeq \omega_{o\to1}$ was assumed. Moreover we would like to show that for those molecules for which the fundamental torsional frequency is silent but the first overtone observed, the barrier heights can be evaluated according to eqs. (1) and (5) of this paper. The results are collected in Table 2.

As far as $\omega_{o\to1}$ is concerned, a comparison between the values of V_3 reported in columns 7 and 9 of Table 2 shows that the procedure here suggested gives a better approximation than the one proposed in ref. 1. Regarding $\omega_{o\to2}$, the values of V_3 (column 8) derived from ω_2^c are in very good agreement with those from MW for the first three molecules. When the splittings of the A and E levels of the second excited torsional state are not negligible, as for the last four molecules in Table 2, the agreement with MW data is better for the E→E transitions, as expected from the results reported in Table 1. Nevertheless, also for these molecules the everaged V_3 value can be considered reasonable.

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