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Computer simulation of the effect exerted by argon matrix on the internal rotation barriers and torsional states of methanol molecule

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Abstract

In the approximation B3LYP/cc-pVTZ, the geometry of a methanol molecule surrounded by eight argon atoms has been optimized. Using a fixed configuration of argon atoms, the internal rotation barriers of methyl and hydroxyl groups, the values of which are compared with that for a free molecule, have been computed. It has been found that insignificant differences in the form of the potential function as compared to a free molecule occur only on rotation of a hydroxyl group, being independent of the methyl group position with respect to the argon lattice. The torsional state energies of a methanol molecule surrounded by argon atoms have been computed taking the difference in the potential functions of the hydroxyl group rotation with respect to the lattice and internal rotation in a free molecule as a perturbing factor. According to the results of these computations, degeneracy of the E-type states is relieved with a slight increase in splitting of the ground torsional state.

Keywords: Internal rotation; Methanol; Matrix isolation; Torsional energy levels

1. Introduction

As demonstrated by the recent studies [1–3], the matrix affects the values of the internal rotation barriers in a methanol molecule, that is reflected by changes in splitting of the torsional states caused mainly by tunneling of a hydroxyl group. Previously [4], in FTIR spectra for methanol recorded at a temperature of 10 K in the argon matrix such an effect has been considered as one of the possible mechanisms responsible for the appearance of a multiplet structure of some absorption bands, in particular a doublet of the bands at 1033.25 and 1036.5 cm^{-1} caused by the valence vibration of C–O bond. At the same time, in the literature we have found no works showing efforts to estimate theoretically the effect of the matrix surroundings on values of the internal-rotation potential barriers and of the torsional transition frequencies in nonrigid molecules. This paper presents a computer simulation of the effect exerted by the surroundings of argon atoms on the torsional motion and positions of the corresponding energy levels in a methanol molecule performed using the package GAMESS [5].

2. Computation method

For recording of low-temperature molecular spectra in the isolated matrix the molecules under study have been initially mixed with argon atoms in a vacuum assembly and only then the mixture came upon the window cooled down to 10 K. Besides, it was supposed that the first stage was associated with the structural formation of the immediate surroundings for the molecule studied. It was assumed that, subsequent to deposition of such clusters on the substrate, the matrix became rigid up to a certain temperature characteristic for every type of the atoms. Proceeding from this hypothesis, a configuration of the complex including a molecule of methanol and eight atoms of argon was optimized at the first stage. Next, the internal rotation barriers were computed at fixed positions of argon atoms. For comparison, the internal-rotation potential function in a free methanol molecule was computed by steps of 20º and the energy level positions for the torsional state were determined. All computations were performed using the quantum-chemical package GAMESS [5] in the approximation B3LYP/cc-pVTZ. The gradient convergence tolerance parameter OPTTOL was set to 10^{-5}.

3. Results and Discussion

3.1. Computation of the torsional states energy for free methanol molecule

To estimate the applicability of B3LYP/cc-pVTZ approximation to computing the potential functions of internal rotation, the torsional state energies for a free methanol molecule have been computed. As noted above, the potential energy of internal rotation with respect to C–O bond was computed at the fixed values of the dihedron H–C–O–H by steps of 20º, the geometry being optimized for all other internal parameters. The computational results are listed in Table 1.

Considering CH_3 group as a symmetric top and O–H atoms — as a frame, we introduce a molecular-fixed system of coordinates with the origin at the molecular center of mass so that the axis c be parallel to the bond C–

Table 1. Internal energy (in a. u.) as a function of the internal rotation angle α.

α	0°	20°	40°	60°	80°
$V(\alpha)$	–115.7043	–115.7047	–115.7055	–115.7060	–115.7056
α	100°	120°	140°	160°	180°
$V(\alpha)$	–115.7047	–115.7043	–115.7047	–115.7055	–115.7060

O (top axis) and the axis *a* perpendicular to the molecular symmetry plane (frame plane). In this case the axis *b* is specified in a unique fashion by the requirement that *a*, *b*, and *c* be forming the right three vectors. Such a selection is conventionally referred to as an internal axes method (IAM) [6–9], the axis *a* being coincident with one of the principle axes of inertia for the whole molecule. In the process of internal rotation in this system of coordinates the inertial parameters of the frame and top are invariable. A classical Hamiltonian for the molecule may be written, most clearly, as follows:

$$H=\frac{1}{2}\begin{pmatrix}\omega_a & \omega_b & \omega_c & \dot{\alpha}+\omega_c\end{pmatrix}\begin{pmatrix}I_{aa} & 0 & 0 & 0\\ 0 & I_{bb} & -I_{bc} & 0\\ 0 & -I_{bc} & I_{fr} & 0\\ 0 & 0 & 0 & I_{\alpha}\end{pmatrix}\begin{pmatrix}\omega_a\\ \omega_b\\ \omega_c\\ \dot{\alpha}+\omega_c\end{pmatrix}+V(\alpha) . \tag{1}$$

However, to go to the momentum representation, we better write expression (1) as

$$H=\frac{1}{2}\begin{pmatrix}\omega_a & \omega_b & \omega_c & \dot{\alpha}\end{pmatrix}\begin{pmatrix}I_{aa} & 0 & 0 & 0\\ 0 & I_{bb} & -I_{bc} & 0\\ 0 & -I_{bc} & I_{cc} & I_{\alpha}\\ 0 & 0 & I_{\alpha} & I_{\alpha}\end{pmatrix}\begin{pmatrix}\omega_a\\ \omega_b\\ \omega_c\\ \dot{\alpha}\end{pmatrix}+V(\alpha) , \tag{2}$$

where ω_a, ω_b, ω_c — projections of the rotation angular rate of the molecule as a whole about the axis of the coordinate system; $\dot{\alpha}$ — angular rotation rate of the top relative to the frame; I_{aa}, I_{bb}, I_{bc}, I_{cc} — inertia tensor elements of the molecule as a whole in the system (*a*, *b*, *c*); I_α — moment of inertia of the top about its symmetry axis; and $I_{fr} = I_{cc} - I_\alpha$. The tensor of inertia in (2) may be made analytically inverse. As a result, we get a classical Hamiltonian in the momentum representation:

$$H=\frac{1}{2}\begin{pmatrix}P_a & P_b & P_c & p\end{pmatrix}\begin{pmatrix}\frac{1}{I_{aa}} & 0 & 0 & 0\\ 0 & \frac{I_{cc}-I_a}{d} & \frac{I_{bc}}{d} & -\frac{I_{bc}}{d}\\ 0 & \frac{I_{bc}}{d} & \frac{I_{bb}}{d} & -\frac{I_{bb}}{d}\\ 0 & -\frac{I_{bc}}{d} & -\frac{I_{bb}}{d} & \frac{I_{bb}I_{cc}-I_{bc}^2}{I_a d}\end{pmatrix}\begin{pmatrix}P_a\\ P_b\\ P_c\\ p\end{pmatrix}+V(\alpha) , \tag{3}$$

where

$$d=I_{bb}I_{cc}-I_{bb}I_{\alpha}-I_{bc}^2 . \tag{4}$$

As coordinate axes are rigidly related to the frame, the top possesses the symmetry C_{3v}, elements of the inverse tensor of inertia are independent of the top rotations with respect to the frame. Because of this, we can change a classical Hamiltonian by the quantum-mechanical one using a simple substitution of the corresponding operators for the classical momenta in (3).

As the Hamiltonian in (3) involves the terms $P_b p$ and $P_c p$, there is no separation between the internal and external rotations in a molecule. Formally, this separation may be attained by the following transformation of the momenta:

$$p'=p-\frac{I_{bc}I_{\alpha}}{I_{bb}I_{cc}-I_{bc}^2}P_b-\frac{I_{bb}I_{\alpha}}{I_{bb}I_{cc}-I_{bc}^2}P_c . \tag{5}$$

In so doing (3) takes the form:

$$\hat{H}=\frac{1}{2}\begin{pmatrix}P_a & P_b & P_c & p'\end{pmatrix}\begin{pmatrix}\frac{1}{I_{aa}} & 0 & 0 & 0\\ 0 & \frac{I_{cc}}{I_{bb}I_{cc}-I_{bc}^2} & \frac{I_{bc}}{2(I_{bb}I_{cc}-I_{bc}^2)} & 0\\ 0 & \frac{I_{bc}}{2(I_{bb}I_{cc}-I_{bc}^2)} & \frac{I_{bb}}{I_{bb}I_{cc}-I_{bc}^2} & 0\\ 0 & 0 & 0 & \frac{I_{bb}I_{cc}-I_{bc}^2}{I_a d}\end{pmatrix}\begin{pmatrix}P_a\\ P_b\\ P_c\\ p'\end{pmatrix}+V(\alpha) . \tag{6}$$

Since there is no rotation of the molecule as a whole in matrix, one can abstract from subsequent steps for complete separation of two rotation types, writing a torsional equation of the form:

$$\frac{I_{bb}I_{cc}-I_{bc}^2}{2I_{\alpha}d}p'^2\Psi+V(\alpha)\Psi=E\Psi , \tag{7}$$

where

$$p'=-i\hbar\frac{\partial}{\partial\alpha} . \tag{8}$$

The effective internal-rotation constant may be transformed to:

$$F=\frac{I_{bb}I_{cc}-I_{bc}^2}{2I_{\alpha}d}=\frac{I_{bb}I_{cc}-I_{bc}^2}{2I_{\alpha}(I_{bb}I_{cc}-I_{bb}I_{\alpha}-I_{bc}^2)}=\frac{1}{2rI_{\alpha}} , \tag{9}$$

where

$$r=\frac{I_{bb}I_{cc}-I_{bb}I_{\alpha}-I_{bc}^2}{I_{bb}I_{cc}-I_{bc}^2}=1-\frac{I_{bb}I_{\alpha}}{I_{bb}I_{cc}-I_{bc}^2} \tag{10}$$

A value of r is easily computed in a system of the principle axes of inertia (*x*, *y*, *z*) whose positions, according to the data of GAMESS computations, are shown in Figure 1. As the axes *a* and *z* care coincident, the axis *c* is nearly coincident with the axis *x*, whereas the axis *b* is directed almost in the opposite direction to the axis *y*, we have:

$$I_{bb}=\gamma_{bx}^2 I_x+\gamma_{by}^2 I_y , \tag{11}$$

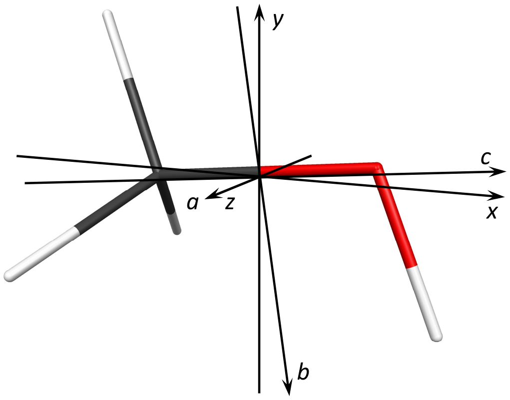

Figure 1. Methanol molecule with the directions of coordinate axes.

where γ_{ij} — direction cosine between the *i*-th axis of the internal coordinate system and the *j*-th principle axis of inertia. Besides, the following equality is valid:

$$I_{bb}I_{cc} - I_{bc}^2 = I_x I_y \,. \tag{12}$$

Taking into account a relative position of the axes (Figure 1), we can clearly see that $\gamma_{by}^2 = \gamma_{cx}^2$ and $\gamma_{bx}^2 = \gamma_{cy}^2 = \cos^2(\arccos\gamma_{cz} + \pi/2)$. Then (10) takes the form:

$$r = 1 - \frac{I_{bb}I_\alpha}{I_{bb}I_{cc} - I_{bc}^2} = 1 - \frac{(\gamma_{bx}^2 I_x + \gamma_{by}^2 I_y)I_\alpha}{I_x I_y} = 1 - \frac{\gamma_{cy}^2 I_\alpha}{I_y} - \frac{\gamma_{cx}^2 I_\alpha}{I_x} \,. \tag{13}$$

Values of the direction cosine γ_{cx}, principal moments of inertia, and effective internal-rotation constant F were computed based on the data of quantum-mechanical computations for the optimized molecular geometry: $\gamma_{cx} = 0.9985$, $I_x = 3.9276\ amu \cdot \text{Å}^2$, $I_y = 20.4214\ amu \cdot \text{Å}^2$, $I_z = 21.1549\ amu \cdot \text{Å}^2$, $F = 27.2642\ \text{cm}^{-1}$.

The potential energy function computed with GAMESS may be approximated by the expression of the form:

$$V(\alpha) = \frac{1}{2}\sum_{m=0}^{3} V_m (e^{i3m\alpha} + e^{-i3m\alpha}) \,, \tag{14}$$

where $V_0 = 185.504$, $V_1 = 185.886$, $V_2 = 0.472$, and $V_3 = 0.090\ \text{cm}^{-1}$. The computed value for the potential barrier height turns to be $V(0) = 371.952\ \text{cm}^{-1}$. This value is in a perfect agreement with the value $372.22 \pm 0.21\ \text{cm}^{-1}$ obtained in [10] using the frequencies of the torsional-rotational spectrum for a methanol molecule. With due regard for symmetry of the potential energy $V(\alpha) = V(\alpha + \frac{2\pi}{3}k)$, where $k = 0;\ \pm 1;\ \pm 2;\ldots$, solutions for equation (7) should be sought in the basis of the eigenfunctions for a free rotator as follows [11, 12]:

$$\Psi_\sigma = \sum_{k=-\infty}^{\infty} A_{3k} e^{i\sigma} e^{i3k\alpha} \,, \tag{15}$$

where σ = 0; ±1. Each torsional energy level, labeled with the quantum number τ (τ = 1, 2, …), is split into three sublevels characterized by the quantum number σ. The case when σ = 0 is associated with nondegenerate energy levels of the *A*-type interpreted as vibrational motions within a potential well. The case when σ = ±1 is associated with the doubly degenerate energy levels of the *E*-type caused by tunneling through the barrier. Substituting (15), (14), and (9)–(13) into equation (7), we derive a system of linear equations with respect to the Fourier series-expansion (15). In the simplest case of a potential of the form $V(\alpha) = V_0(1 + \cos 3\alpha)$ for nondegenerate states $(\sigma = 0)$ such a system may be generated by the following equation:

$$(E' - 9k^2 - 2V_0')A_{3k} + V_0' A_{3(k-1)} + V_0' A_{3(k+1)} = 0 \,, \tag{16}$$

where $E' = \frac{E}{F}$ and $2V_0' = \frac{V_0}{F}$. Then eigenvalues of the energy $E_{\tau\sigma}$ and eigenfunctions expansion coefficients A_{3k} are found by diagonalization of the matrix the fragment of which is given in (17):

$$\begin{array}{cccccccccc}
3k & \rightarrow & -9 & -6 & -3 & 0 & 3 & 6 & 9 & \ldots \\
\downarrow & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \\
-9 & \ldots & -2V_0'-81 & V_0' & 0 & 0 & 0 & 0 & 0 & \cdots \\
-6 & \ldots & V_0' & -2V_0'-36 & V_0' & 0 & 0 & 0 & 0 & \cdots \\
-3 & \ldots & 0 & V_0' & -2V_0'-9 & V_0' & 0 & 0 & 0 & \cdots \\
0 & \ldots & 0 & 0 & V_0' & -2V_0' & V_0' & 0 & 0 & \cdots \\
3 & \ldots & 0 & 0 & 0 & V_0' & -2V_0'-9 & V_0' & 0 & \cdots \\
6 & \ldots & 0 & 0 & 0 & 0 & V_0' & -2V_0'-36 & V_0' & \cdots \\
9 & \ldots & 0 & 0 & 0 & 0 & 0 & V_0' & -2V_0'-81 & \cdots \\
\vdots & & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots
\end{array} \tag{17}$$

Since the infinite matrices must be truncated for numerical computation, the accuracy of the eigenvalues was checked by comparing the results from matrices of increasing order. The matrix, which had a size 123x123, was numerically diagonalized and eigenvalues are found. Table 2 presents the calculated and experimental energies [13, 14] of lower torsional states for a free molecule of methanol. The potential function of internal rotation $V(\alpha) - V_{\min}$ and positions of the torsional states for τ = 1 and 2,3 are shown in Figure 2, *a*. Note that the computed splitting of the ground torsional state (8.87 cm^{-1}) is in a perfect agreement with the data [13, 14] on splitting of the ground torsional state in the case of a free molecule of CH_3OH (9.12 cm^{-1}), pointing to the applicability of the approximation B3LYP/cc-pVTZ to computations of both the potential barriers of internal rotation and molecular geometric parameters.

Table 2. The energy values for lower torsional states of a free methanol molecule.

τ	σ	Symmetry species	Energy $E_{\tau\sigma}$, cm^{-1}		Energy difference $E_{\tau\sigma} - E_{10}$, cm^{-1}	
			Calculated	Experimental	Calculated	Experimental
1	0	*A*	127.10	127.98	0.	0.
	±1	*E*	135.97	137.10	8.87	9.12
2	±1	*E*	334.61	336.89	207.51	208.91
	0	*A*	419.04	422.43	291.94	294.45
3	0	*A*	477.60	481.19	350.50	353.22
	±1	*E*	633.68	638.30	506.58	510.32
4	±1	*E*	874.19	879.02	747.08	751.04
	0	*A*	1171.58	1174.64	1044.48	1046.66

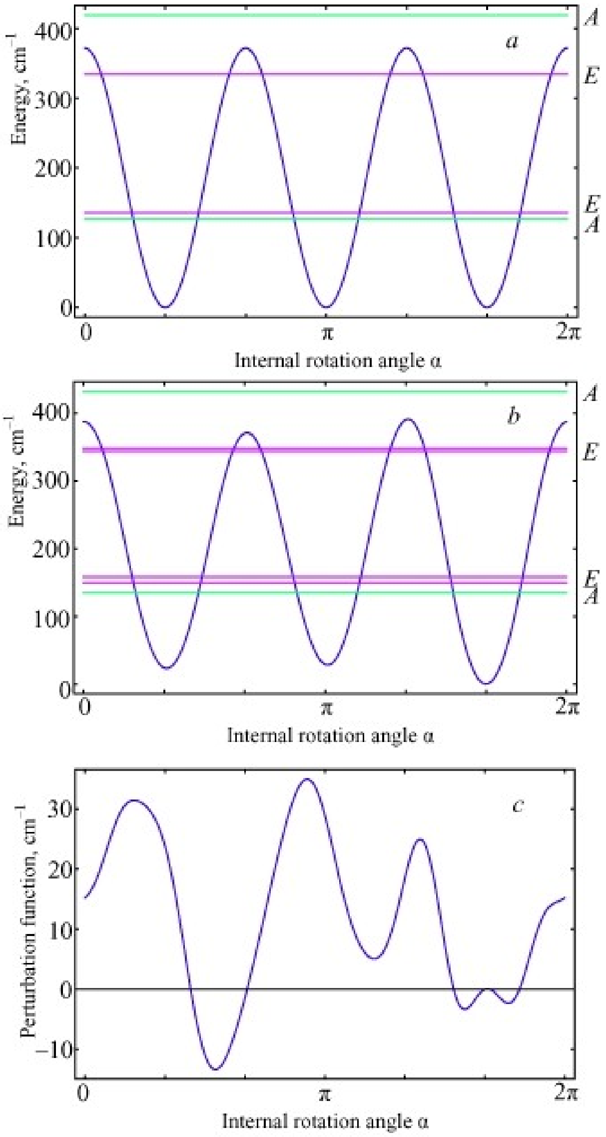

Figure 2. The internal-rotation potential energy function f1(α) of a free methanol molecule and positions of lower torsional energy levels (a); the internal-rotation potential energy function f3(α) and positions of lower torsional energy levels (b); difference between the functions f3(α) – f1(α) (c).

3.2. Computation of the torsional states energy for methanol molecule in argon matrix

Proceeding from the above, the configuration including a molecule of methanol and eight argon atoms, initially positioned at the vertices of the cube, was first optimized for all the internal parameters. The optimized configuration is shown in Figure 3. In the optimized configuration the argon atoms were kept fixed in space. Then rotation of methyl and hydroxyl groups with respect to the argon lattice was performed. As it was found that the internal forces originating in a methanol molecule were greater than the interacting forces with the matrix, on optimization for all the parameters characterizing a position of CH_3OH molecule in the matrix, the methyl group rotation relative to the argon lattice was accompanied by the hydroxyl group rotation, and vice versa. Because of this, in the case of a methyl group rotation by steps of 20º the hydroxyl group position was additionally fixed relative to the matrix, and vice versa - for rotation of a hydroxyl group the position of a methyl group was fixed. Besides, all other internal parameters of CH_3OH were optimized.

Next we introduce three functions of the form $f_t(\alpha) = V_t(\alpha) - V_t^{\min}$ where t =1, 2, 3. Indices 1, 2, and 3 characterize the potential energy function for internal rotation of a free molecule, rotation of methyl and hydroxyl groups relative to the matrix, respectively. All the functions were defined with respect to the internal rotation angle. We are of the opinion that, apart from convenience of joint comparative analysis, such functions offer the possibility of partial compensation for BSSE (basis set superposition error) effect [15] known as leading to artificial overestimation of the binding energy between the fragments of dimeric and polymeric molecular systems in the case of insufficiently complete base set. It should be noted that difference between the functions $f_2(\alpha) - f_1(\alpha)$ is close to zero for any value of the angle α, whereas $f_3(\alpha) - f_1(\alpha)$ is clearly other than zero (Figures. 2, *b* and *c*). This stems from the differences in symmetries of CH_3 and OH groups. Higher symmetry of a methyl group makes it possible to considerably remove asymmetry in the positions of argon atoms, that is not so in the

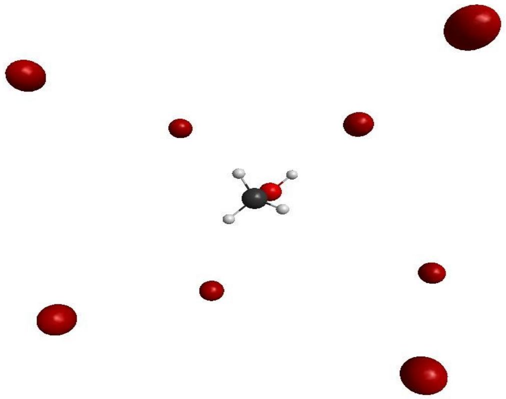

Figure 3. The optimized configuration of a methanol molecule complex with argon atoms.

case of a hydroxyl group. An exact solution of the problem about an internal rotation of methanol in the argon matrix may be derived only by computing the two-dimensional potential surface and by solving the two-dimensional Schrödinger equation. At the same time, one can calculate approximately the shift of the torsional energy levels that is due to the interactions between the methanol molecule and argon matrix, taking equation (7) as a Schrödinger equation in the zeroth-order approximation and the function, $f_3(\alpha)-f_1(\alpha)$ — as a perturbation operator. Since the wave functions in the zeroth-order approximation are known from solution of equation (7), corrections to the energy in the first approximation of a perturbation theory are of the form:

$$\Delta E^{(1)}_{\tau\sigma}=\int_0^{2\pi}\Psi_{\tau\sigma}(\alpha)(f_3(\alpha)-f_1(\alpha))\Psi^*_{\tau\sigma}(\alpha)d\alpha\,. \qquad (18)$$

Involvement of higher orders in a perturbation theory enables more accurate estimates of the effects exerted by perturbation. The matrix elements of the Hamiltonian are numerically calculated in an set of basis functions $\Psi_{\tau\sigma}$. The Hamiltonian matrix of dimension 90x90 was sufficient to stabilize the energy values of the lower torsional states. This matrix was numerically diagonalized and eigenvalues were found. The computed corrections and new energies are listed in Table 3.

According to the computational results obtained, splitting of the ground torsional state is somewhat increased. Besides, splitting of the *E*-type degenerate states occurs due to the relieved degeneracy. Based on these data, we can suggest that a mechanism of a multiplet splitting of some absorption bands in low-temperature FTIR spectra for methanol in the argon matrix [4] is not associated with the matrix effect on the parameters of the internal rotation barrier, and its nature is different.

4. Conclusions

Despite the fact that an increased splitting of the ground state of a methanol molecule in the argon matrix is somewhat unexpected, it may be qualitatively explained. When a molecule of methanol is trapped into the argon matrix, initially equivalent three potential barriers are deformed to different extents on rotation of a hydroxyl group that, as has been already noted, is mainly responsible for internal rotation of the molecule. The height of one of the barriers increases, whereas that of two other barriers is decreased. As a result, the probability of tunneling is growing, that leads to the increased splitting of the ground torsional state. Besides, clockwise and counter-clockwise internal rotations become nonequivalent to relieve degeneracy and to effect splitting of the *E*-states. But an increase in the height of one of the barriers may be considered a factor hindering rotation of the molecule as a whole. The computed perturbations are not large and mainly affect the energy levels which are close to deformations of the barrier (close to maxima and minima of the potential curves). This is in accord with the results obtained too.

Table 3. Computed energies of lower torsional states for a methanol molecule with regard to perturbation in the argon matrix.

τ	σ	Symmetry species	$E^{(0)}_{\tau\sigma}$, cm^{-1}	$\Delta E^{(1)}_{\tau\sigma}$, cm^{-1}	$\Delta E^{(n)}_{\tau\sigma}$, cm^{-1}	$E^{(1)}_{\tau\sigma}$, cm^{-1}	$E^{(n)}_{\tau\sigma}$, cm^{-1}	$E^{(n)}_{\tau\sigma}-E^{(n)}_{10}$, cm^{-1}
1	0	*A*	127.10	14.72	7.94	141.82	135.03	0.
	±1	*E*	135.97	14.94 15.01	13.53 22.08	150.91 150.98	149.50 158.05	14.47 23.02
2	±1	*E*	334.60	11.95 11.95	10.43 13.35	346.56 346.56	345.04 347.96	210.00 212.92
	0	*A*	419.04	12.61	12.69	431.65	431.74	296.70
3	0	*A*	477.60	12.07	12.31	489.67	489.92	354.88
	±1	*E*	633.68	12.51 12.51	12.28 12.98	646.19 646.19	645.95 646.65	510.92 511.62
4	±1	*E*	874.18	12.65 12.65	12.45 12.98	886.83 886.83	886.63 887.16	751.60 752.12
	0	A	1171.58	12.74	12.78	1184.32	1184.36	1049.33

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References

1. Y.-P. Lee, Y.-J. Wu, R.M. Lees, L.-H. Xu, J.T. Hougen., Science 311 (2006) 365.
2. J.P. Perchard., J. Chem. Phys. 332 (2007) 86.
3. J.P. Perchard, F. Romain, Y. Bouteiller., Chem. Phys. 343 (2008) 35.
4. G.A. Pitsevich, I.Yu. Doroshenko, V.Ye. Pogorelov, D.S. Umrejko., J. Spectrosc. Dyn. 1 (2011) 9.
5. http://www.msg.ameslab.gov/GAMESS/GAMESS.html
6. H.H. Nielsen., Phys. Rev. 40 (1932) 445.
7. D.G. Burkhard, D.M. Dennison., Phys. Rev. 84 (1951) 408.
8. K.T. Hecht, D.M. Dennison., J. Chem. Phys. 26 (1957) 31.
9. C.C. Lin, J.D. Swalen., Rev. Mod. Phys. 31 (1959) 841.
10. Y.Y. Kwan, D.M. Dennison., J. Mol. Spectrosc. 43 (1972) 291.
11. E.T. Whittaker, G.N. Watson., Modern Analysis, Fourth (Edn.), Cambridge (1958) pp. 404-429.
12. H. Jeffreys, B. Swirles., Methods of Mathematical Physics. Third (Edn.), Cambridge, Cambridge University Press, Vol. 3 (1966) pp. 23-30.
13. G. Moruzzi, P.Riminucci, F. Strumia, B.Carli, M.Carlotti, R.M. Lees, I. Mukhopadhyay, J.W.C. Johns, B.P. Winnewisser, M. Winnewisser., J. Mol. Spectrosc. 144 (1990) 139.
14. G. Moruzzi, F. Strumia, J. Moraes, R.M. Lees, I. Mukhopadhyay, J.W.C. Johns, B.P., Winnewisser, M. Winnewisser., J. Mol. Spectrosc. 153 (1992) 511.
15. S.F. Boys, F. Bernardi., Mol. Phys. 19 (1970) 553.

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