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The predicted value of potential barrier to internal rotation of benzaldehyde: is there a conflict between the theory and the experiment or not?

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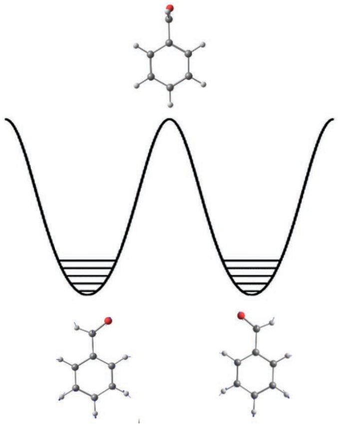
The ratio of potential barrier heights for the internal rotation of benzaldehyde molecule calculated by quantum mechanical methods and determined experimentally from UV spectra has been discussed. Based on the joint analysis of the results of *ab initio* MP2/6-311G calculations of normal vibrations of benzaldehyde in the ground state and the results of interpretation of the observed UV spectra of the compound, possible approximations for a correct description of the hindered internal rotation of the aldehyde group have been considered. The two-dimensional model including the kinematic interaction between torsion and out-of-plane deformation of aldehyde group has been established as more efficient for the correct description of the hindered rotation in benzaldehyde.**



Keywords: benzaldehyde, potential barrier to internal rotation, experimental torsion energy levels, two-dimensional model, quantum chemical calculations, matrix elements of vibration kinetic energy.

Quantum chemical methods are widely used for calculations of the heights of potential barriers to the internal rotation of molecules.[1–10] In many cases, modern quantum mechanical methods allow one to estimate the heights of potential barriers close to the corresponding ‘experimental’ ones or to predict the large amplitude vibrations and give new insights into the molecular structure and dynamics.[8,11] Investigations of the certain molecules possessing internal rotation[12–14] have demonstrated that the torsional barriers and fundamental frequencies for large amplitude motions can be accurately predicted within MP2 theory and extended basis sets if the geometry relaxation is allowed. The single-rotor torsional barriers of acetone,[12] ethanol[13] and acetic acid[14] have been determined as equal to 267.1, 1296.3 and 169.8 cm^{-1}, which are close to the experimental values of 266.1, 1251 and 168.2 cm^{-1}.[12–14]

Due to the growing number of quantitative predictions made on the basis of various quantum chemistry software packages, the discussion of new results often requires additional calculations and analyses. Consideration of internal rotations in polyatomic molecules is one of the complicated problems in the molecular spectroscopy. The reliability and accuracy of the models and methods used are evaluated by comparing the calculated values of the energy barrier height with the corresponding ‘experimental’ ones. The latter can be obtained on the basis of spectral data processing by solving the inverse problem with using the energies of torsional vibration levels. Though sometimes we have been encountering with an unexpected discrepancy between calculation and experiment, *e.g.*, a decrease in the torsion barrier due to steric hindrance.[11]

An example of such discrepancy is the height of potential barrier to internal rotation of benzaldehyde, C_6H_5CHO. For this molecule, the theoretical barrier values estimated within different levels of theory were up to 2 times higher than the experimental values. The first experimental determination of the height of potential barrier to internal rotation of benzaldehyde molecule[15] was based on solving the inverse torsion problem *via* experimental IR torsion energy level (110.85 cm^{-1}) within the framework of Pitzer’s model[16] and included an estimate of the reduced moment of inertia for given molecular geometry in the one-dimensional (1D) approximation. The estimated height of potential barrier[15] was equal to 4.61 kcal mol^{-1} (1611 cm^{-1}). In one of the later theoretical calculations of benzaldehyde,[17] where the potential barrier height has been calculated using various density functional theory (DFT) methods and extrapolation procedure, the barrier height was determined as 2690 cm^{-1} (7.7 kcal mol^{-1}). The authors[17] regarded this result as a ‘conflict’ between the theory and the experimental deductions.

In this work, we have reviewed the reasons for the differences between calculated and ‘empirical’ values of the barrier height, in particular, the reliability and accuracy of all obtained data, both calculated and experimental. Besides, we have analysed the influence of some kinematic factors on the barrier height in benzaldehyde molecule associated with large amplitude motions.

The origin of the significant discrepancies between the experimentally determined and quantum mechanical calculated values of the potential barrier has been discussed for more than twenty years.[18–22] Our study[23] led to the conclusion that this discrepancy could be due to both the erroneous interpretation of torsional energy levels above the first one[15] and a significant kinematic interaction of torsion and out-of-plane deformation of CHO group in the benzaldehyde molecule which has not been considered in the one-parameter model. It has been shown[23] that the reassignment of some levels of torsion and inclusion the above mentioned kinematic interaction of two vibrations in the analysis [*i.e.*, determining the potential function of internal rotation in a two-dimensional (2D) approximation] allows obtaining the calculated value of the barrier height close to the results of most quantum mechanical calculations. At the same time, the calculated energies of torsion transitions and out-of-plane deformation of the CHO group satisfactorily reproduced the corresponding experimental data.[23]

However, more recently, the high-resolution Fourier-transform infrared (FTIR) spectrum of benzaldehyde has been obtained.[24] The torsional fundamental 109.415429(20) cm^{-1} was identified *via* rovibrational analysis (while earlier, the value of 110.85 cm^{-1} was proposed[15]) and followed by the tentative assignment of the hot torsion transitions (2←1) and (3←2) to 107.58 cm^{-1} and 105.61 cm^{-1}, respectively. Previously, these two transitions were measured[15] at 109.51 and 106.52 cm^{-1}, though later they were assigned in a different way.[25]

Based on the assignment of these first three torsion transitions, the potential function of internal rotation was determined[24] in 1D approximation and the barrier to internal rotation was estimated as 1533.6 cm^{-1} (4.38 kcal mol^{-1}), contrary to values of 2878.1 cm^{-1} (8.23 kcal mol^{-1}) (MP2/cc-pVTZ) and 2777.2 cm^{-1} (7.94 kcal mol^{-1}) (CCSD(T)/cc-pVTZ) calculated in the same work. Again, it was noted that the experimental value of the internal rotation barrier in benzaldehyde was still too low and underestimated and the discrepancy between theory and experimental remained despite the experimental efforts.[24] It has been assumed that large difference between the experimental and theoretical values of the internal rotation barrier in benzaldehyde is due to the errors in the experimental data.

We believe that such differencies are caused by the other reasons. The first one is related to the use of a highly simplified the one-parameter model – the so called one-dimensional (1D) approximation. It is well known that the efficiency of this model is largerly determined by how strongly the potential of the rotating top of the molecule depends on other internal vibrations in the analysed system. Thus, the 1D hindered rotor approximation should be used only in the cases when the molecule does not have complex or strongly coupled rotations. The second condition of the accurate using the simplest 1D model is an absence of the strong kinematic coupling between the corresponding terms of the given molecule.[26] In other words, the torsional frequency should be clearly separated from other normal vibrations. Regretably, both of these conditions are not always analysed when choosing the appropriate physical and mathematical model for the quantum mechanical treatment of internal rotation.

Thus, it is obvious that in the case of benzaldehyde it is important to investigate all possible reasons for observed differences between theoretical and empirical potential barrier heights, in particular, accuracy of the model and the reliability of obtained data, both calculated and experimental.

Herein, we consider the importance of taking into account all the above mentioned factors while estimating the energy barrier of hindered internal rotation in the benzaldehyde molecule. To study the kinematic interaction between out-of-plane vibrations of the aldehyde group we use the results of quantum mechanical calculations of benzaldehyde performed in this work by the MP2/6-311G** method, followed by an analysis of molecular normal vibrations in internal coordinates. For reference, similar calculations were carried out for benzoyl fluoride.

Ab initio and DFT calculations have been performed with the program GAUSSIAN 09 (Revision D.01)[27] package. The fully optimized geometry and harmonic force fields of benzaldehyde have been calculated at the HF, MP2 and DFT levels of theory with the 6-31G*, 6-311G**, 6-31+G**, PVTZ basis sets.[28] All calculations have been done without any restrictions on the symmetry of structure. The minima of the potential surface were found by relaxing the geometric parameters with the standard optimization methods. Analytical force constants were derived and harmonic vibrational frequencies were calculated at all aforementioned theoretical levels. The visualization of results has been made using Chemcraft software (version 1.8).[29] Finally, for the detailed interpretation of vibrational spectra we have used the results of calculations carried out at the MP2/6-311G** level.

Data on optimized geometry (Table S2, Online Supplementary Materials) and vibrational frequencies (Table 1) obtained at this level of theory had been consistent with experimental geometry[30] and spectra.[31] The optimized configuration of benzaldehyde with numbering of used atoms is shown in Figure S1. The ground state Hessian (obtained at the MP2/6-311G** level of theory) of benzaldehyde was transformed to the force constant matrix in redundant internal coordinates in the frame of the canonical matrix model.[32–34] The redundant system of internal coordinates includes coordinates for all bond stretches (14 coordinates) and all bond angles (22 coordinates) (36 so called ‘planar’ coordinates in total) that were generated automatically *via* special root of the SPECTRUM program.[32] The set of non-planar internal coordinates of benzaldehyde molecule includes: seven out-of-plane bending ones related to the type 3 (five coordinates for CH groups in benzene ring, one out-of-plane C–H bending for the aldehyde group, one C–C out-of-plane bending for C–C(O)H fragment) and seven torsional coordinates, six of them being torsions around C–C bonds in the benzene fragment and the torsion of the aldehyde group (Table S3). Eventually, the redundant system of internal coordinates of benzaldehyde molecule includes 49 internal coordinates (14 coordinates of bond stretches, 21 coordinates of bond angles, 7 out-of-plane coordinates and 7 torsional coordinates. The definition of introduced internal coordinates of a molecule is shown in Table S3. Potential energy distribution (PED) values have been calculated in accordance with the previously described formula.[35] Comparison of theoretical and observed frequencies of benzaldehyde and calculated potential energy distribution on vibrations is presented in Table 1. These data demonstrate satisfactory description of observed vibrational spectra by the chosen theoretical level taking into account the anharmonicity of the experimental spectra.

The potential energy distribution data in Table 1 confirm the complicated character of molecular vibrations in benzaldehyde, especially in the low-frequency region. We have compared the lowest three frequencies in the theoretical spectra of benzaldehyde and benzoyl fluoride.

Obviously, due to the large difference between masses of hydrogen and oxygen atoms in the CHO group the amplitudes of out-of-plane vibration of this group with containing hydrogen atom are significantly larger than amplitude of oxygen atom. As a result, this vibration includes a partially torsion motion. The cross terms in the matrix of kinetic energy *G* of the benzaldehyde molecule which correspond to the non-planar coordinates for aldehyde group are large values (Table S4).

According to the calculated PED, the theoretical frequency of benzaldehyde should be assigned to the torsional vibration of the aldehyde group (with contribution of about 62%) (see Figure 1); PED of this frequency also includes parts from two other non-

Table 1 Comparison of calculated at the MP2/6-311G** level of theory normal frequencies of benzaldehyde molecule with observed in vibrational spectra (S_0 state).

Vapour[a]	Liquid[a]	MP2/6-311G**	Symmetry[b]	PED (%)
3099		3234	A′	36(qq2) 31(qq3) 20(qq4) 12(qq5)
3081		3228	A′	39(qq5) 37(qq2) 19(qq4) 3(qq6)
3081		3218	A′	31(qq3) 30(qq5) 21(qq2) 15(qq4) 4(qq6)
3043		3207	A′	43(qq4) 36(qq3) 10(qq6) 6(qq2) 6(qq5)
3034		3195	A′	82(qq6) 13(qq5) 3(qq4)
2806		2945	A′	100(qCH)
1728	1730	1761	A′	87(qCO) 4(aHCC) 3(QQ1)
1614		1649	A′	22(Q2) 22(Q5) 8(Q6) 7(Q1) 5(Q3)
1603	1601	1633	A′	18(Q1) 18(Q6) 18(Q4) 16(Q3) 4(A4)
		1521	A′	12(A3) 11(B5) 10(A6) 9(B2) 6(B3)
1460		1483	A′	15(B4) 12(A4) 11(A5) 8(B3) 6(Q5)
		1463	A′	17(Q2) 16(Q4) 15(Q5) 14(Q3) 11(Q1)
1387		1424	A′	45(aHCO) 24(aHCC) 4(Q1) 4(Q6) 3(qCO)
1314		1331	A′	17(A2) 15(B6) 12(B2) 11(A3) 8(A6)
1276		1238	A′	36(QQ1) 9(Q2) 8(Q5) 6(Q6) 5(G1)
1202	1204	1190	A′	14(A6) 13(B6) 12(A5) 10(B5) 9(B2)
1168	1172	1182	A′	22(B4) 20(A4) 13(B3) 11(A3) 8(Q3)
1074		1100	A′	18(B2) 14(Q5) 12(A6) 9(Q2) 8(B5)
1026	1028	1043	A′	20(Q3) 19(Q4) 9(A2) 8(B3) 8(A5)
	996	1014	A″	93(XH) 3(XX)
		1005	A′	9(Q1) 8(Q6) 8(G5) 8(G2) 7(G3)
		918	A″	25(T2) 24(X3) 22(X2) 9(X5) 6(T3)
		903	A″	26(T4) 20(X4) 19(T3) 13(X5) 11(T5)
		880	A″	21(X4) 21(T5) 18(X6) 13(X2) 9(X5)
825	829	838	A″	27(X6) 18(X2) 17(X3) 11(X5) 8(T6)
		837	A′	20(QQ1) 19(Q1) 14(G4) 12(aOCC) 7(aHCC)
740		724	A″	24(X5) 22(X4) 20(X3) 13(X6) 10(X2)
688 c	652	656	A′	25(aOCC) 12(G4) 10(b1c) 8(aHCC) 7(Q6)
	617	619	A′	18(G3) 15(G6) 15(G5) 12(G2) 6(B3)
649	437	437	A′	24(QQ1) 19(G1) 17(a1c) 6(G2) 6(aOCC)
450		430	A″	43(XX) 17(T4) 16(X4) 13(T3) 3(X5)
		407	A″	19(XX) 15(X2) 14(X6) 14(X3) 12(X5)
		389	A″	21(T5) 19(T2) 10(X6) 9(X3) 9(T3)
224	224	227	A″	30(Tors) 23(T1) 16(T6) 11(XX) 6(X2)
217		219	A′	39(b1c) 31(a1c) 15(aOCC) 7(aHCC)
111		113	A″	62(Tors) 12(XX) 10(T6) 6(T1) 4(XH)

[a] Data from ref. 31. [b] Description of internal coordinates is given in Table S3.

planar vibrations – the C–C out-of-plane deformations for aldehyde group (12%) and cycle torsion (10%).

The potential energy distribution calculated for the frequency of 228 cm^{-1} also demonstrates the contribution of the same vibrations with more strong contributions from two torsional vibrations of the benzene ring adjacent to the aldehyde group. According to the PED calculations, the third of the lowest frequencies at 219 cm^{-1} (located between two frequencies considered) is related to the so called planar vibrations. It includes the in-plane deformations of valence angles, it has no contributions from out-of-plane vibrations and should be assigned to the deformations of C1–C2–C3 and C1–C2–C4 valence angles.

These results on the potential energy distribution for two low frequencies of benzaldehyde and their mean square amplitudes (see Table S5) demonstrate rather strong coupling between the contributions of so called non-planar coordinates into the amplitudes of low-frequency vibrations and confirm the necessity to use at least 2D model for the analysis of hindered rotation of aldehyde group.

Calculated at the MP2/6-311G** level of theory three lowest vibrations of benzoyl fluoride as well as the corresponding distributions of potential energy are shown in Figure 2.

In this case, the masses of O and F atoms are close and the amplitude of corresponding out-of-plane vibration becomes similar to amplitude of ‘classic’ wagging one (*i.e.*, similar to

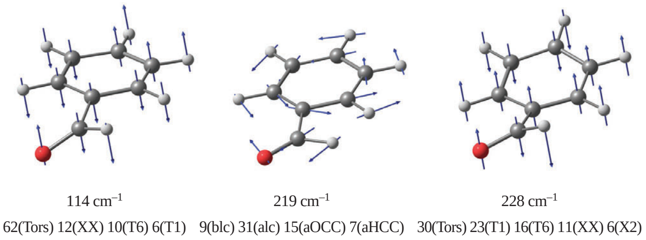


Figure 1 Visualized low frequency vibrations for benzaldehyde (MP2/6-311G**).

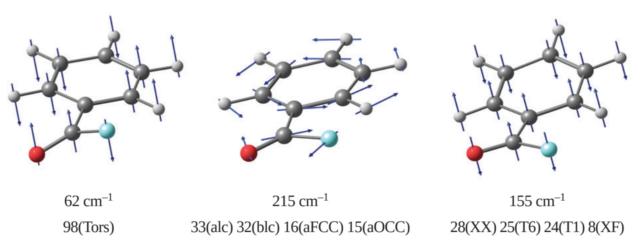


Figure 2 Visualized low frequency vibrations for benzoyl fluoride (MP2/6-311G**).

wagging of CX_2 group). In contrast to benzaldehyde molecule (Figure 2), the potential energy distribution for torsional vibration practically does not have crossing terms between torsion and wagging vibrations of CXY group in the full matrix *G* and, correspondingly, it has no contributions to the potential energy distributions of low frequency vibrations. This conclusion has been supported by calculations of mean square amplitudes of two molecules under consideration (see Table 2 and Table S5) where the amplitudes of valence angles in pairs HCO–FCO and HCC–FCC are compared.

Obviously, the torsion and out-of-plane vibrations XH in both molecules are characterized by large amplitudes of vibrations but mean square amplitudes for HCO and FCO angles as well as for HCC and FCC angles are significantly different. These data confirm the conclusion regarding the difference between kinematic models of hindered rotation in benzaldehyde and benzoyl fluoride, *i.e.*, for the fluoro-substituted molecule the kinematic interactions of torsional vibration with other vibrations are weaker than similar interactions in benzaldehyde.

Further, we consider how the results for the ground state discussed above agree with the results of applying various models for the analysis of hindered internal rotation in benzaldehyde based on electronic-vibrational spectra obtained earlier,[25] where one-dimensional and two-dimensional sections of the potential energy surface were used based on the torsion and out-of-plane CHO deformation. Calculated and experimental energies of torsion and out-of-plane CHO deformation for benzaldehyde molecule (in the ground S_0 state) torsion transitions assignments are presented in Table S1. The experimental data is based on the assignments of the torsion transitions proposed earlier,[15,23,25] though the frequencies are partially different.

The results of investigation of low-resolution far infrared spectrum[15] as well as our results are presented in the Table S6. The reassignments of three torsion transitions higher than the first one (*i.e.*, 108.51, 106.52 and 104.17 cm^{-1}, respectively) were proposed in our publication.[23] Previously,[15] such assignment of torsion transitions was rejected because of the relatively close distance between successive electronic states. The incorrect interpretation of the spectra proposed in that work resulted in the significant overestimation of the potential barrier.

The tentative assignment of the energies of two (hot) torsion transitions (107.58 and 105.61 cm^{-1}) has been done in examining FTIR spectrum of benzaldehyde[24] (Table S6). We assume that these values should be reassigned to the other hot transitions, similar to the suggested earlier.[23] Moreover, there was no assignment[24] of the most intense band near 110.85 cm^{-1}, which was earlier interpreted as fundamental torsion.[15] All three versions of the assignments are shown in Table S6. The results of applying 1D model undoubtedly demonstrate significant disagreements with all corresponding experimental data both for torsion and out-of-plane CHO deformations[15,23,24] and do not match with relevant harmonic values (Table S6).

Table 2 Comparison of mean square amplitudes (calculated at the MP2-6-311G** level of theory) for the aldehyde groups of benzaldehyde and benzoyl fluoride.

Benzaldehyde			Benzoyl fluoride		
Coordinate	*T* = 0 K	*T* = 293 K	Coordinate	*T* = 0 K	*T* = 293 K
qCH	0.0785 Å	0.0785 Å	qCF	0.0460 Å	0.0465 Å
qCO	0.0375 Å	0.0376 Å	qCO	0.0364 Å	0.0364 Å
aHCO	6.3163°	6.3336°	aFCO	3.7062°	3.8270°
Tors	7.5441°	12.0249°	Tors	5.6634°	14.0569°
aHCC	6.2923°	6.3843°	aFCC	3.3395°	3.6243°
aOCC	3.7872°	4.0383°	aOCC	3.8161°	4.0679°
XH	8.8542°	8.9978°	XF	6.9605°	7.3086°

Earlier,[23] the results of MP2/6-311G** calculations have also been used for the analysis of potential energy surface (PES) within the framework of a two-dimensional (2D) model ($\tau = 0°$, $\chi = 0°$, where τ and χ are coordinates of internal rotation and out-of-plane CHO deformation, respectively). In the minimum of 2D potential energy surface (PES) the elements of kinematic matrix $\|B_{ij}(\tau,\chi)\|$ have been obtained[23] as equal to $B_{11} = 2.67$, $B_{22} = 1.17$ and $B_{12} = 0.94\ \text{cm}^{-1}$. The height of potential barrier to internal rotation calculated in 2D approximation is equal to 2870 cm^{-1} (8.2 kcal mol^{-1})[23] and is close to typical theoretical results for this value 2690 cm^{-1} (7.7 kcal mol^{-1}).[22] The calculated energies of torsion and out-of-plane CHO deformation transitions in 1D and 2D approximations are shown in the Table S1. One can see that agreement between calculated experimental energies is quite satisfactory for 2D (but not for the 1D) model. Thus, basing on the data shown in Tables S1, 2 and S3 we can assume that for the benzaldehyde molecule the analysis of hindered internal rotation of aldehyde group within 1D approximation is not appropriate. The results of our calculations[23] have demonstrated the significant kinematic interaction between torsion and out-of-plane deformation vibrations of aldehyde fragment that is not related to the features of the 1D potential.

It allows us to draw a conclusion that analysis of spectra within 2-D model[23] correlates well with the results obtained here for the ground state of benzaldehyde at the MP2/6-311G** level of theory. Analysis of the elements of the full matrix of kinetic energy *G* for benzaldehyde molecule demonstrates the large values for the cross off-diagonal terms between torsional (Tors) and out-of-plane (XH) coordinates.

According to the results of calculation within the two-dimensional model,[23] the interaction between torsion and out-of-plane CHO deformation is also significant, the values of kinematic coefficients B_{12} and B_{22} are close.[23] The similar effect was also observed in investigation of furfural and some other five-member heterocyclic aromatic aldehydes.[25]

Seeing that the construction of the two-dimensional quantum mechanical model is a difficult problem, it would be tempting to use simpler approaches for the preliminary analysis of the more complex physical model than one-dimensional for molecules with hindered internal rotation. That would allow one to detect the out-of-plane molecular vibrations that have a kinematic and/or dynamic relationship with torsional vibrations and formulation of the physical model for the constructing the multidimensional quantum mechanical model for the hindered rotation in this molecule. Hence, the results of *ab initio* MP2/6-311G** calculations of optimized structure and harmonic frequencies of benzaldehyde are in good compliance with the experimental spectral data. Data processing within the full kinematic model confirms the conclusions of 2-D/MP2/6-311G** analysis[23] for the hindered internal rotation of this molecule.

The importance of using the extended (at least 2D) model for the analysis of hindered internal rotation in benzaldehyde molecule is well supported by the analysis of matrix of kinetic energy *G* of benzaldehyde in the ground state. It demonstrates the strong couplings terms between two non-planar [CH(O)-out-of-plane and torsional] vibrations in benzaldehyde confirmed by the results of normal coordinate analysis (Table 1). Together these data support the conclusion that the hindered rotation of the aldehyde group in the benzaldehyde molecule should be analyzed at least within a two-dimensional model taking into account significant kinematic interaction between the torsional and out-of-plane deformation vibrations of the CHO group.

To sum up, comparative analysis of the identified torsional transitions in observed UV spectra and results of quantum mechanical calculations within three theoretical models for benzaldehyde molecule allows us to conclude that the number of torsion energy levels in the potential hole is determined by the depth of potential well. If the potential barrier to internal rotation is high, that is, the potential well is deep (~2700–2800 cm^{-1}), one may expect the presence in the well of a sufficiently large number of torsion energy levels, more than twenty-five. Therefore, the energies of subsequent torsion transitions can decrease slowly. The adequate agreement was found between the experimental torsion energy levels proposed in our assignment and those calculated within 2D model. It means that they are nearly harmonic, so the assignment is quite resonable. Thus, when analysing the barrier for applying hindered rotation in benzaldehyde, we observed a satisfactory complience between the calculated and experimental energies of both torsion and out-of-plane CHO deformation in the case of 2D calculation, but not for 1D calculation.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.06.044.

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