THE JOURNAL OF
PHYSICAL CHEMISTRY A

Article

pubs.acs.org/JPCA

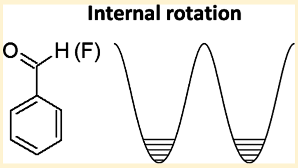
# The Barriers to Internal Rotation of Benzaldehyde and Benzoyl Fluoride: "Reconciliation" Between Theory and Experiment

Igor A. Godunov,* Vadim A. Bataev, Alexander V. Abramenkov, and Vladimir I. Pupyshev

Chemistry Department, Lomonosov Moscow State University, 119991, Moscow, Russia

*Supporting Information*

**ABSTRACT:** This work is devoted to investigation of the known problem of the discrepancy between the experimental and theoretical values for the barrier to internal rotation of the molecules comprised of a benzene ring and a $\pi$-conjugated substituent, such as benzaldehyde and benzoyl fluoride. The possible reasons of such discrepancy are considered. As a result the conclusion was drawn that the origin of the problem is incorrectness of the assignments of the torsional levels higher than first, both for benzaldehyde and benzoyl fluoride. In addition the significant kinematic interaction between torsional vibration and out-of-plane CHO deformation was found for benzaldehyde.



## I. INTRODUCTION

Nowadays, quantum chemistry is a quite reliable tool for studying and predicting molecular systems properties. Modern high-level quantum chemical methods make it possible to calculate the molecular parameters very close to corresponding experimental values. Nevertheless sometimes we come across the cases of unexpected disagreement between calculated and experimental values. It is important to understand the origin of such disagreement: is it some limitation of quantum chemical methods or does there exist some incorrectness of experimental value determination?

The vivid example of the discrepancy mentioned between the theoretical and experimental values is the potential barrier to internal rotation of benzaldehyde molecule, $C_6H_5CHO$ (and, possibly, of molecules comprising a benzene ring with a $\pi$-conjugated substituent). Compared to experimental values, the theoretical ones (in particular, calculated using density functional theory (DFT) and some other quantum chemical methods) are of up to a factor 2 too high.

There are three works where the values of benzaldehyde rotational barrier were determined using experimental data. Miller, Fateley, and Witkowski[1] observed torsional band at 111 cm$^{-1}$ in the gas-phase infrared spectrum of benzaldehyde and calculated the barrier to internal rotation as 4.66 kcal/mol (1630 cm$^{-1}$). Then Kakar, Rinehart, Quade, and Kojima[2] investigated the microwave spectra of benzaldehyde and its isotopomer $C_6H_5CDO$. Relative intensities of rotational transitions measurements gave the torsional frequencies of $113.8 \pm 5.0$ cm$^{-1}$ for $C_6H_5CHO$ and $108.4 \pm 4.25$ cm$^{-1}$ for $C_6H_5CDO$.[2] The barriers to internal rotation calculated from these frequencies were $4.90 \pm 0.43$ ($1714 \pm 150$ cm$^{-1}$) and $5.28 \pm 0.42$ ($1847 \pm 147$ cm$^{-1}$) kcal/mol for $C_6H_5CHO$ and $C_6H_5CDO$, respectively.[2] At last Durig, Bist, Furic, Qui, and Little[3] studied far-infrared (FIR) spectrum of gaseous benzaldehyde. The fundamental CHO torsion for benzaldehyde was assigned to 110.85 cm$^{-1}$ with three consecutive vibrational transitions to more excited states at 109.51, 106.52, and 104.17 cm$^{-1}$. These data allowed for determination of the potential function of internal rotation of the benzaldehyde, and the rotational barrier was found to be 4.61 kcal/mol (1611 cm$^{-1}$).[3]

The rotational barrier determinations in the works[1−3] were based on one-dimensional (1D) approximation for internal rotation and Pitzer's model[4] for evaluation of the reduced moment of inertia for given molecular geometry. One can see that all experimental results[1−3] are in close agreement with one another.

Later, the rotational barrier heights were calculated using various DFT and *ab initio* quantum chemical methods. The results and discussion can be seen in the works.[5−13] As a rule, calculated values essentially exceeded experimental ones.

Meier et al.[5,7,9], based on their results, drew the conclusion that the molecular systems comprising a benzene ring with a $\pi$-conjugated substituent form a special problem with respect to calculation of the rotational barrier around the C(sp$^2$)—C(aryl) bond. DFT functionals cannot properly handle such barriers.

On the other hand Head-Gordon and Pople[6] calculated the rotational barriers for six conjugated ethylenes and six analogous substituted benzenes using *ab initio* methods (HF/6-31G**//HF/6-31G* and MP2/6-311G**//HF/6-31G*) with agreement as a rule of better than 1 kcal/mol between the calculations and experiment. Three molecules were the exception: nitrobenzene, benzaldehyde, and benzoyl fluoride (in particular, the rotation barrier for benzaldehyde was equal to 8.282 kcal/mol, which was ~3 kcal/mol higher than experimental values). Head-Gordon and Pople supposed that theoretical values were to be preferred for these systems.[6,8]

At last, Speakman, Papas, Woodcock, and Schaefer III[10] carried out careful calculations of the benzaldehyde rotational

**Received:** April 7, 2014
**Revised:** October 11, 2014

barrier (in particular, using extrapolation procedure) and concluded that the main reason for the discrepancy between calculated and experimental values was the use of Pitzers's model for the computation of the reduced moment of inertia, which could not be applied to such conjugated molecule with asymmetric rotators as benzaldehyde though there was no problem with calculations of the system with a nonconjugated functional group, such as phenol molecule.[10] Experimental values of the benzaldehyde rotational barrier are therefore misleading, and the true rotational barrier lies closer to the theoretically extrapolated limit of 7.7 kcal/mol (2690 $cm^{-1}$), based on coupled cluster theory.[10] The authors of this paper[10] named the problem described above "conflict between theory and experimental deductions".

A similar disagreement between calculated and experimental heights of potential barrier to internal rotation was observed for the related molecule of benzoyl fluoride, $C_6H_5CFO$.

From the relative intensity measurements in the microwave spectrum of benzoyl fluoride Kakar[14] determined the torsional frequency to be 59.5 ± 3 $cm^{-1}$ and then the barrier to internal rotation of 4.46 kcal/mol (1560 ± 160 $cm^{-1}$). Later Durig at al.[3] obtained the far-infrared spectrum of benzoyl fluoride and observed two bands, 63.36 and 61.91 $cm^{-1}$. They assigned the stronger band at 63.36 $cm^{-1}$ to the $1 \leftarrow 0$ torsional transition and the weaker band at 61.91 $cm^{-1}$ to the $2 \leftarrow 1$ transition, and they determined the height of potential barrier to be 4.97 kcal/mol (1739 $cm^{-1}$) in accordance to Kakar value.[14] However, Larsen, Pedersen, and Sørensen[15] examined the microwave spectrum of 4-fluorobenzoyl fluoride, and in the discussion they did not agree with the band assignments in the far-infrared spectrum of benzoyl fluoride presented by Durig et al.[3] They argued that the $2 \leftarrow 1$ transition should be stronger than the fundamental (of roughly half the intensity). In addition Larsen et al.[15] indicated that all their observations and Kakar's[14] as well supposed the harmonic behavior of the torsional potential. Therefore, they supposed that the stronger band was a superposition of a number of transitions: $1 \leftarrow 0$, $2 \leftarrow 1$, etc. and that the weaker was a hot band of similar composition.[15]

Taking into account only $V_2$ term (in the Fourier series expanding of the potential function of internal rotation) Larsen et al.[15] obtained the height of potential barrier to be 4.49 kcal/mol (1569 $cm^{-1}$). But assuming that the far-infrared band 63.36 $cm^{-1}$ could be superposition of all torsional transitions from $1 \leftarrow 0$ to $5 \leftarrow 4$ and including of $V_4$ Fourier term (estimated as −164(3) $cm^{-1}$) Larsen et al.[15] obtained the height of potential barrier as 6.7 kcal/mol (2345(10) $cm^{-1}$) in agreement with calculated value 7.301 kcal/mol.[6] It is worth noting, however, that the last estimation[15] of potential barrier is assumed rather than proven.

In our work we analyzed the possible origins of the discrepancy between calculated and experimental heights of potential barriers to internal rotation of benzaldehyde and benzoyl fluoride molecules. In particular, we paid attention to the adequacy of the calculating method and the correctness of the assignments of experimental torsional frequencies. In addition we examined the possibility of the internal rotation interaction with some other molecular internal motions.

As a result we concluded that the origin of the discrepancy between theoretical and experimental values of potential barrier to internal rotation of benzaldehyde and benzoyl fluoride consists in some errors of the torsional bands assignments in the spectra. In addition the second origin was found for benzaldehyde—the kinematic interaction between internal rotation and out-of-plane deformation of the CHO group.

As indicated above, the third molecule that demonstrated the discrepancy between calculated and experimental values of potential barrier was nitrobenzene (4.838 as against 2.8 kcal/mol, respectively).[6] Recently the molecular structure of nitrobenzene was reinvestigated,[16] and the experimental barrier height was estimated to be in the region of 4.1−4.6 kcal/mol, in accordance with the theoretical value.[6] However, it seems that some additional comments are needed.

## II. COMPUTATIONAL DETAILS

At first, we performed the quantum chemical calculations. We used, as a rule, the standard MP2/6-311G** approximation. The calculations were performed with the MOLPRO 2010.1 quantum-chemistry program package.[17] The geometrical parameters, vibrational frequencies, and parameters of the potential functions of internal rotation were calculated.

Moreover the geometries and force-field parameters of benzaldehyde were estimated within MP2/cc-pVTZ approximation. All results obtained are presented in Tables S1 and S2; see Supporting Information. One can see that, on the whole, the calculated parameters are in reasonable agreement with one another and with known experimental data. In addition some calculations were carried out using multiconfigurational methods CASSCF and CASPT2 with def2-TZVPP basis set.[18] Active space in our calculations includes 11 molecular orbitals (MOs) ($4\pi + \sigma_{CO} + n_O + 4\pi^* + \sigma_{CO}^*$) with 12 electrons distributed on them.

Next, the direct torsional problems were solved for the quantum chemical potential functions of internal rotation. The coordinates used for the nuclear motion analysis are defined here in the following way (see Figure 1 for the atomic nuclei numeration). The coordinate $\tau$ of CHO-group rotation is defined with the help of additional dummy atoms $Q_1$ and $Q_2$. Both the segments of a straight lines $Q_1C_1$ and $Q_2C_7$ are orthogonal to the bond $C_1C_7$. The point $Q_1$ belongs to the plane ($C_6C_1C_2$), while the point $Q_2$ belongs to the plane ($H_1C_7O$). The internal rotation coordinate $\tau$ is defined as the dihedral angle $\angle Q_1C_1C_7Q_2$. The coordinate $\chi$ for out-of-plane CHO deformational vibration is the angle of the bond $C_1C_7$ with the plane ($C_6C_1C_2$).

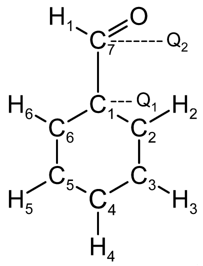


**Figure 1.** Numbering of the atoms in the molecule of benzaldehyde. The dummy atoms $Q_1$ and $Q_2$ used to set the internal rotation coordinate (see the text) are also depicted.

We used the computer program[19] similar to that described by Lewis et al.[20] in which the 1D vibrational Schrödinger equation was solved variationally with the Hamiltonian of the form

$$H(\tau) = -\frac{\partial}{\partial\tau}B(\tau)\frac{\partial}{\partial\tau} + V(\tau) \tag{1}$$

where $\tau$ is the coordinate of internal rotation. $B(\tau)$ is the internal rotation kinematic function

$$B(\tau) = B_0 + \sum_n B_n \cos n\tau \tag{2}$$

and $V(\tau)$ is the potential function of internal rotation

$$V(\tau) = \frac{1}{2}\sum_n V_n(1 - \cos n\tau) \tag{3}$$

In some cases the two-dimensional (2D) direct problems were solved for internal rotation and out-of-plane CHO or CFO motion. In these cases the vibrational Hamiltonian has the following form:

$$\begin{aligned} H_{2D} = & -\frac{\partial}{\partial\tau}B_{11}(\tau,\chi)\frac{\partial}{\partial\tau} - \frac{\partial}{\partial\chi}B_{21}(\tau,\chi)\frac{\partial}{\partial\tau} \\ & - \frac{\partial}{\partial\tau}B_{12}(\tau,\chi)\frac{\partial}{\partial\chi} - \frac{\partial}{\partial\chi}B_{22}(\tau,\chi)\frac{\partial}{\partial\chi} + V(\tau,\chi) \end{aligned} \tag{4}$$

where $B_{ij} = B_{ij}(\tau,\chi)$ are the elements of the hermitian 2 × 2 kinematical matrix and $V$ is the potential function. The indexes 1, 2 correspond to the coordinates of internal rotation ($\tau$) and out-of-plane CHO (or CFO) motion ($\chi$), correspondingly. $V$ and $B_{ij}$ functions were approximated by linear combinations of the multiplicative trigonometric functions of variables $\tau$ and $\chi$ that ensure the symmetry of potential energy surface (PES) and kinematical parameters $B_{ij}$. The solution of the variational problem was realized by the Rayleigh−Ritz linear variational method with the trigonometric functions basis set.

In addition the inverse torsional problems were solved using the computer program.[19] On the basis of experimental energy levels of torsional vibrations, the "experimental" potential functions of internal rotation were determined.

## III. RESULTS AND DISCUSSION

**III.1. Benzaldehyde.** *III.1.1. Experimental Potential Function of Internal Rotation.* The authors of ref 3 observed in the far-infrared spectrum the four groups of torsional transitions, which are presented in Table 1 with their assignment (left column). However, it is not hard to see that another version of the assignment (right column) is also possible. Moreover, this version of the torsional transitions assignment was considered by the authors of ref 3 and rejected "because of the relative close spacing of the successive transitions" (the consequence of such assignment is the high potential barrier, but in that time the problem of the disagreement of the calculated and experimental values of benzaldehyde potential barrier was not discussed yet).

Using the assignment of four torsional transitions presented in the right column of Table 1 and experimental geometrical parameters[21,22] from the Table S1 (Supporting Information), we obtained the parameters of $B(\tau)$ and $V(\tau)$ functions for benzaldehyde (in cm$^{-1}$). Namely, calculating three and four parameters in (3) we obtained

$$B_0 = 1.832,\ B_2 = 0.092,\ B_4 = 0.003$$

$$V_2 = 2500,\ V_4 = -290,\ V_6 = 30$$

$$V_2 = 2720,\ V_4 = -410,\ V_6 = 70,\ V_8 = -7$$

respectively.

Table 1. Observed[a] Bands in FIR Spectrum of Benzaldhyde and Their Alternative Assignments

| | | assignments | |
|---|---|---|---|
| $\nu$ (cm$^{-1}$) | relative intensity | work[a] | this work[b] |
| 110.85 | m | 1←0 torsion | 1←0 torsion |
| 110.55 | mw | hot band | 2←1 torsion |
| 110.28 | mw | hot band | 3←2 torsion |
| 110.05 | w | hot band | 4←3 torsion |
| 109.51 | m | 2←1 torsion | $(\nu_x + \nu_{tors})\leftarrow\nu_x$ |
| 109.25 | w | hot band | $(\nu_x + 2\nu_{tors})\leftarrow(\nu_x + \nu_{tors})$ |
| 107.65 | w | hot band | hot band |
| 106.52 | w | 3←2 torsion | $(\nu_y + \nu_{tors})\leftarrow\nu_y$ |
| 106.23 | w | hot band | $(\nu_y + 2\nu_{tors})\leftarrow(\nu_y + \nu_{tors})$ |
| 105.85 | vw | hot band | $(\nu_y + 3\nu_{tors})\leftarrow(\nu_y + 2\nu_{tors})$ |
| 105.64 | w | hot band | $(\nu_y + 4\nu_{tors})\leftarrow(\nu_y + 3\nu_{tors})$ |
| 105.13 | vw | hot band | hot band |
| 104.17 | w | 4←3 torsion | $(\nu_z + \nu_{tors})\leftarrow\nu_z$ |

[a] Far infrared spectrum, ref 3. [b] The hot bands are assigned to combinational transitions, where $\nu_x$, $\nu_y$, and $\nu_z$ are likely low-frequency bending fundamentals.

The potential barriers to internal rotation for functions with three and four parameters are equal to 2530 cm$^{-1}$ (7.2 kcal/mol) and 2790 cm$^{-1}$ (8.0 kcal/mol), respectively. That is, the experimental and calculated[10] values are of the same order. Thus, reassignments of the torsional transitions in comparison with the work[3] permitted the obtainment of good agreement between calculated (refs 6 and 10) and experimental heights of benzaldehyde potential barrier to internal rotation.

*III.1.2. Calculated Potential Function of Internal Rotation.* Within the MP2/6-311G** approximation the parameters of the $B(\tau)$ and $V(\tau)$ functions are as follows (in cm$^{-1}$):

$$B_0 = 1.802,\ B_2 = 0.105,\ B_4 = 0.008 \tag{5}$$

$$V_2 = 2880,\ V_4 = -80,\ V_6 = -10 \tag{6}$$

and the potential barrier for this function is 2870 cm$^{-1}$ (8.2 kcal/mol). The calculated barrier height is in agreement with the value of 2690 cm$^{-1}$ (7.7 kcal/mol) obtained by Speakman et al.[10] using extrapolation of the quantum chemical results to the complete basis set, in considerable disagreement with earlier experimental barrier of 1611 cm$^{-1}$ (4.61 kcal/mol).[3]

However, the comparison of only the potential barriers is not sufficient to draw a reliable conclusion about agreement or disagreement between the calculated and experimental internal rotation hindered potentials. In addition it is necessary to compare the calculated and experimental energies of torsional vibrational levels, which are depend on both the height of potential barrier and the form of potential function.

Therefore, using the parameters (5) and (6), we calculated the energy of torsional levels, see Table 2 (1D MP2 calculations). One can see from Table 2 that 1D energies of torsional levels are badly agreed with experimental values (for example, the 1D calculated energy of torsional frequency, 137 cm$^{-1}$, is more far from the experimental one, 110.85 cm$^{-1}$, than calculated harmonic frequency,[23] 113 cm$^{-1}$, Table S2).

It is worth noting that calculations of the vibrational (harmonic) frequencies using both MP2/6-311G** and MP2/cc-pVTZ methods proved the significant coupling of the torsional vibration and out-of-plane CHO deformation.

**Table 2. Calculated and Experimental Energies ($\mathrm{cm^{-1}}$) of Torsional Levels of Benzaldehyde**

| | MP2[b] | | CASSCF[c] | | CASPT2[d] | | |
|---|---|---|---|---|---|---|---|
| torsional level[a] | 1D | 2D | 1D | 2D | 1D | 2D | expt[e] |
| 1 | 137 | 112 | 124 | 110 | 132 | 112 | 110.85 |
| 2 | 273 | 224 | 246 | 220 | 262 | 224 | 221.40 |
| 3 | 408 | 336 | 367 | 328 | 392 | 336 | 331.68 |
| 4 | 541 | 448 | 486 | 436 | 520 | 448 | 441.73 |
| $\nu_{35}$[f] | 142 | 208 | 177 | 220 | 161 | 220 | 223.8[g] |

[a] All the torsional levels presented are doubly degenerate ones. [b] Calculated by MP2/6-311G** (torsion harmonic frequency 113 $\mathrm{cm^{-1}}$). [c] Calculated by CASSCF(12e-11MO)/def2-TZVPP (torsion harmonic frequency 109 $\mathrm{cm^{-1}}$). [d] Calculated by CASPT2//CASSCF-(12e-11MO)/def2-TZVPP. [e] Calculated by summarizing of torsional transition energies from Table 1 (right column). [f] Out-of-plane CHO deformation (harmonic frequencies 228 and 238 $\mathrm{cm^{-1}}$ for MP2/6-311G** and CASSCF/def2-TZVPP, respectively). [g] Reference 3.

Interaction of these vibrational modes was studied in 2D approximation.

The 2D section of PES is shown in Figure 2. One can see that the motion along rotational coordinate $\tau$ leads to very small changes of the nonplanar coordinate $\chi$. Therefore, these two motions can be analyzed separately when only the form of PES is studied.

But for vibrational problem the good separation of motions along coordinates $\tau$ and $\chi$ is possible if the kinematical matrix $\|B_{ij}(\tau,\chi)\|$ is almost diagonal. At the minimum point ($\tau = 0°$, $\chi = 0°$) we calculated $B_{11} = 2.67$, $B_{22} = 1.17$, $B_{12} = 0.94\ \mathrm{cm^{-1}}$. The relatively large value of $B_{12}$ demonstrated the essential role of the kinematic interaction of the motions under consideration in the vicinity of minimum.

Table 2 shows the results of solving 2D vibrational problem (2D MP2 calculations). One can see that the consideration of coordinates $(\tau,\chi)$ interaction provides good agreement between calculated and experimental energies of vibrational levels. Moreover, contrasting with the 1D calculation, the 2D approximation provides good agreement between calculated and experimental energies of out-of-plane CHO deformation vibration.

*III.1.3. Multiconfiguration Calculations.* Meier et al.[5,12] claimed that an adequate theoretical description of the rotational barrier height in benzaldehyde required the inclusion of nondynamic electron correlation within the MCSCF-type but not the MP2-type method. These authors carried out such calculations[5] on the basis of the complete active space (CAS(8)) and the restricted active space (RAS(14)), using ANO-type basis sets for fixed geometric parameters of planar (minimum) and perpendicular (barrier) conformations obtained by RHF/6-31G*. As a result, they obtained the heights of 5.0 (for CAS(8)) and 4.3 (for RAS(14)) kcal/mol in agreement with experimental values of the earlier works.[1−3]

But recently Burcl[13] carried out the calculations of the benzaldehyde rotation barrier height using a number of methods: CCSD(T) and CR-CC(2,3) in cc-pVXZ (X = D, T) basis sets, MCSCF in vdz/vdzp and cc-pVTZ basis sets, CASPT2(8)/cc-pVTZ, and some others (for example, CASPT2(8)/cc-pVTZ yields a rotation barrier of 7.6 kcal/mol). The results obtained demonstrated that (i) nondynamic correlation plays only a minimal role in the description of this problem and (ii) the earlier MCSCF data (i.e., the calculations by Meier et al.[5]) significantly underestimated the magnitude of the barrier, likely due to imbalance in active spaces of minimum and transition-state geometry.[13]

In our work we calculated 1D and 2D sections of PES by CASSCF and CASPT2 methods using def2-TZVPP basis set. Then we solved 1D and 2D vibrational problems, and the results are also presented in Table 2.

It can be seen that calculated by CASPT2 the values of the energies of four lower torsional levels, taking into account both dynamic and nondynamic electron correlation, are in very good agreement (in the case of the 2D model, the result is practically identical) with MP2/6-31G** results.

Note that calculated barrier heights (2269 $\mathrm{cm^{-1}}$ or 6.5 kcal/mol for CASSCF/def2-TZVPP and 2667 $\mathrm{cm^{-1}}$ or 7.6 kcal/mol for CASPT2//CASSCF/def2-TZVPP) differ considerably from the estimates presented in ref 5, while the difference between CASPT2 data obtained by Burcl[13] and the results of extrapolation[10] is not more than 0.1 kcal/mol.

Our results confirm the conclusions by Burcl[13] and point out that the data obtained for benzaldehyde by modern multi-

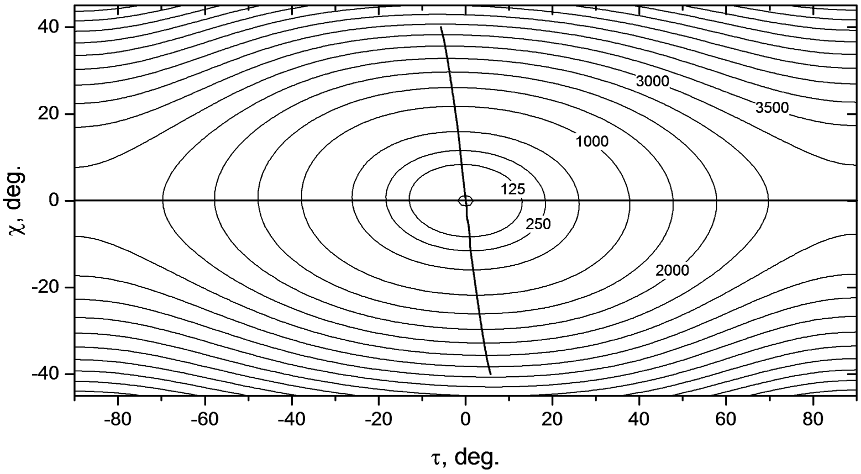


**Figure 2.** Two-dimensional cross section of PES (in $\mathrm{cm^{-1}}$) for the benzaldehyde molecule, estimated in MP2/6-311G** approximation. The detailed definition of coordinates see in the text: $\tau$ = coordinate of the internal rotation, $\chi$ = out-of-plane CHO deformation coordinate. The solid lines indicate the one-coordinate minimal energy path.

configurational methods (not only potential barrier heights but also energies of torsional levels) are in agreement with corresponding MP2 data, and all of them are close to the experimental values in our assignments of the far-infrared spectrum.

**III.2. Benzoyl Fluoride.** The geometrical parameters calculated using MP2/6-311G** method are presented in the Table S3 (Supporting Information). The corresponding experimental parameters are unknown, but calculated and experimental rotational constants are in good agreement. The calculated vibrational frequencies are in satisfactory agreement with experimental ones,[24] but in contrast to benzaldehyde, the PED analysis shows that the torsional vibration does not interact (practically) with any other vibrations. The testing of relative molecules Ph−CX(=Y) shows that one can wait the significant kinematic interaction between torsional vibration and out-of-plane CXY deformation in that case when the masses of atoms X and Y differ strongly. In the case of benzoyl fluoride the masses of oxygen and fluorine are close.

The parameters of the potential function of internal rotation of benzoyl fluoride calculated by MP2/6-311G** method are as follows (in cm$^{-1}$):

$$V_2 = 2530,\ V_4 = -165,\ V_6 = -10$$

and the height of the potential barrier to internal rotation for this function is equal to 2515 cm$^{-1}$ (7.2 kcal/mol), which is in good agreement with calculated value[6] of 7.301 kcal/mol and exceeds the experimental[3,14] one.

We calculated the energies of torsional levels of benzoyl fluoride in 1D approximation, Table 3. In addition we present in Table 3 the results of 2D approximation (torsional and out-of-plane CFO deformation section) for comparison with benzaldehyde.

**Table 3. Calculated and Experimental Energies (cm$^{-1}$) of Torsional Levels of Benzoyl Fluoride**

| | calculated[a] | | experimental | | | |
|---|---|---|---|---|---|---|
| torsional level | 1D | 2D | MW[b] | MW[c] | UV[d] | FIR[e] |
| 1 | 64 | 64 | 59.5 ± 3 | 60.03 | 57 | 63.36 |
| 2 | 129 | 127 | 117 ± 7 | | 115 | (125.27)[f] |
| 3 | 193 | 191 | 177 ± 10 | | 171 | |

[a] See notes for Table 2. [b] Microwave spectrum.[14] [c] Microwave spectrum.[15] [d] Ultraviolet spectrum.[25] [e] Far-infrared spectrum.[3] [f] Sum of (1 ← 0) and (2 ← 1) torsional transitions.[3] In this work we suggest another assignment; see text.

One can see from Table 3 that, in accordance with benzaldehyde, 1D and 2D calculated energies are near harmonic, and in contrast with those of benzaldehyde, they are similar. It is not surprising, as for benzoyl fluoride molecule the masses of X and Y atomic nuclei are essentially similar, and this results in small values of nondiagonal matrix elements of kinematical matrix. Therefore, the 1D approximation may be used without essential errors.

The results of our calculations are in agreement with the assumption of Larsen et al.[15] that the strong band of 63.36 cm$^{-1}$ in far-infrared spectrum[3] is a superposition of a number of torsional transitions (1 ← 0, 2 ← 1, etc.).

However, this conclusion disagrees with results of analysis of benzoyl fluoride $S_1 \leftarrow S_0$ ultraviolet spectrum by Balfour,[25] who assigned the bands progression of 57, 117, and 171 cm$^{-1}$ to torsional vibronic transitions: 0 ← 1, 0 ← 2, and 0 ← 3, respectively; see Table 3. Therefore, we considered the Balfour's assignment once again.

Balfour[25] indicated that all bands in the ultraviolet spectrum were double-headed with a head separation of ~6 cm$^{-1}$, and band measurement referred to the head at lower energy.

However, one may expect that the bands of the $S_1 \leftarrow S_0$ spectrum, corresponding to the vibronic transitions $A_{ev}'' \leftarrow A_{ev}'$ (torsional transitions 0 ← 0 and 0 ← 2) and $A_{ev}'' \leftarrow A_{ev}''$ (torsional transitions 0 ← 1 and 0 ← 3) have distinct rotational contours ($A_{ev}'$ and $A_{ev}''$ are the symmetries of vibronic levels). It could be shown that there are bands of the C-type and (A+B)-type, respectively.[26]

We simulated the rotational contours of vibronic bands[27] of benzoyl fluoride, Figure 3. We used the benzoyl fluoride geometrical parameters in the ground ($S_0$) electronic state from the Table S3 and their relative changes in the excited electronic state ($S_1$) as follows: $\Delta r(C_1{-}C_7) = r'(C_1{-}C_7) - r''(C_1{-}C_7) = -0.11$ Å, $\Delta r(C{=}O) = +0.185$ Å, $\Delta r(C{-}H) = -0.012$ Å, $\Delta\angle CCO = -1.7°$, and $\Delta\angle CCH = 12.0°$. These values were evaluated from our calculations for relative molecules in the ground and excited states: acrolein (CASSCF(8e-7MO)/cc-pVTZ),[28,29] acryloyl fluoride (CASSCF(8e-7MO)/cc-pVTZ), and benzaldehyde (CASSCF(12e-11MO)/cc-pVTZ).

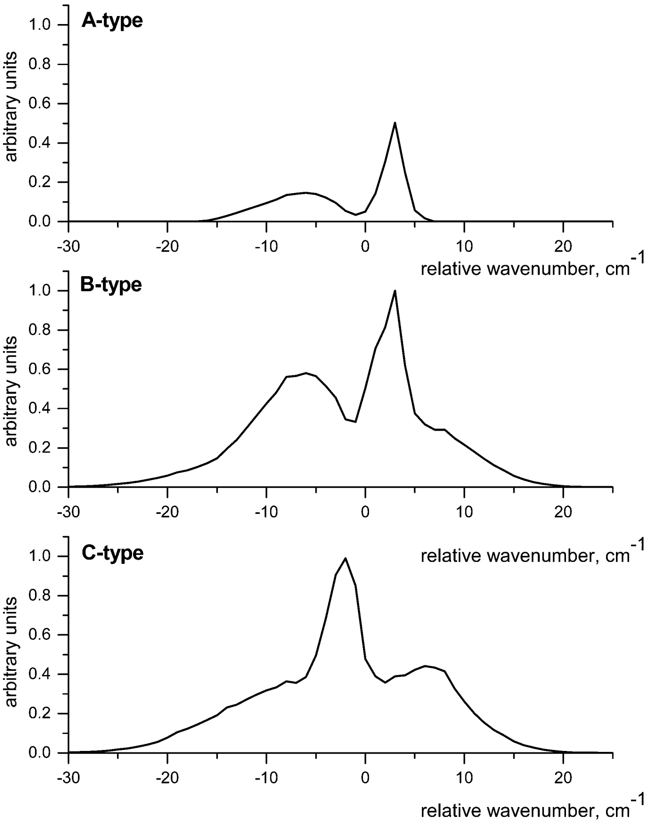


**Figure 3.** Simulated rotational contours of the vibronic bands of benzoyl fluoride: A-, B-, and C-types. Rotational constants (in cm$^{-1}$): $A' = 0.126\,871$, $A'' = 0.127\,223$, $B' = 0.040\,020$, $B'' = 0.040\,384$, $C' = 0.030\,423$ $C'' = 0.030\,654$, slit width = 1 cm$^{-1}$; temperature = 298 K.

One can see in Figure 3 that both (A+B)-type and C-type bands are double-headed with a head separation of ~8 cm$^{-1}$, very similar to bands described by Balfour.[25]

The stronger head for (A+B)-type band is the higher energy one, and the stronger head for C-type band is the lower energy one. The separation between the head of lower energy (Balfour[25] measured these heads) and rotational origin of the vibronic bands ($\nu_{00}$) is ~6 $cm^{-1}$ for (A+B)-type bands and ~2 $cm^{-1}$ for C-type bands. Therefore, the progression of torsional transitions 0 ← 1, 0 ← 2, and 0 ← 3 can not be as regular as it is observed.

The conclusion is that all bands in ultraviolet spectrum[25] have the same rotational contour as $0_0^0$ band—vibrational origin of the electronic transition $A_{ev}'' \leftarrow A_{ev}'$, that is, C-type. (And it is clear that band measurements referred to the more intensive heads at low energy.) Therefore, the pointed progression must be assigned to the sequence 0 ← 0, 1 ← 1, 2 ← 2, and 3 ← 3 of, most probably, in-plane CFO vibration with low frequency (212 $cm^{-1}$).[25]

By the way, this clarifies the reason for the large difference between energies of torsional levels presented in refs 3 and 25 (see Table 3).

Thus, our conclusions are

(i). the far-infrared band of 63.36 $cm^{-1}$ is a superposition of a number of torsional transitions (the calculated values are 63−64 $cm^{-1}$; see Table 3)
(ii). the band of 61.91 $cm^{-1}$ is a relative hot band.
(iii). the height of the potential barrier to internal rotation is near the calculated value of 7.2 kcal/mol.

**III.3. Nitrobenzene.** Head-Gordon and Pople[6] pointed to this molecule as a third example of discrepancy between calculated (4.838 kcal/mol) and experimental (2.8 kcal/mol) potential barriers to internal rotation.

But recently Dorofeeva et al.[16] reinvestigated the molecular structure of nitrobenzene by the method of gas-phase electron diffraction. Those authors[16] used both static and dynamic models and calculated the height of the potential barrier as being in the range of 4.1−4.6 kcal/mol, in accordance with the calculation of ref 6. In particular, Dorofeeva et al.[16] using dynamic model obtained the geometric parameters and the parameters of the potential function of internal rotation (3) as follows (in kcal/mol):

$$V_2 = 4.6 \pm 0.2, V_4 = -1.0 \pm 0.3 \tag{7}$$

Using these data we calculated the torsional frequency of nitrobenzene as 30 $cm^{-1}$ in comparison with the experimental valuations of 49.67 $cm^{-1}$ in the gas phase[30] and 51 $cm^{-1}$ in the liquid phase.[31]

We suppose that the reason for such disagreement is overestimation of $V_4$ value (modulus). Fixing the values of $V_2$ (the height of the potential barrier) and torsional frequency (50 $cm^{-1}$) we estimated the $V_4$ value about of −0.5 kcal/mol, not too far from the value of −1.0 ± 0.3 kcal/mol, evaluated using dynamic model.[16]

## IV. RESULTS AND CONCLUSIONS

The examination of the problem of discrepancy between the experimental and theoretical heights of the potential barriers to internal rotation of molecules comprising of a benzene ring and a $\pi$-conjugated substituent, such as benzaldehyde and benzoyl fluoride molecules, was carried out.

We reanalyzed the experimental far-infrared spectrum of benzaldehyde[3] and found that the assignment of torsional levels more high than the first could be altered. Using new assignment of torsional levels for benzaldehyde, the height of potential barrier to internal rotation was obtained in agreement with the results of most quantum chemical calculations.

In addition to potential barrier heights we compared the calculated and experimental energies of torsional levels. With this purpose, at first stage, we calculated the potential functions of internal rotation of benzaldehyde in 1D (torsion) and 2D (torsion and out-of-plane CHO deformation) approximations using MP2 method and also CASSCF and CASPT2 methods.

On the basis of these potential functions the corresponding 1D and 2D vibrational problems were solved, and the energies of torsional and out-of-plane CHO deformation levels were obtained. The corresponding results obtained for benzaldehyde by different theoretical methods, both one- and multiconfigurational, are in good agreement with each other. This confirms the conclusions by Burcl[13] that the electron correlation plays only a minimal role and that the earlier MCSCF data significantly underestimated the height of potential barrier.

In addition, for benzaldehyde the significant kinematic interaction between torsional vibration and out-of-plane CHO deformation was found. Such significant kinematic interaction can occur if in the molecules $C_6H_5{-}CX({=}Y)$ the masses of atoms X and Y are distinguished strongly, such as oxygen and hydrogen. Altering the assignment of the torsional levels and taking into account the pointed kinematic interaction we obtained the good agreement not only between experimental and calculated potential barrier heights but also between experimental and calculated (2D) energies of torsional levels of benzaldehyde.

For benzoyl fluoride the masses of oxygen and fluorine atoms are close, and any significant interaction between torsional vibration and other vibrations is not observed; therefore, 1D and 2D energies of torsional levels are practically the same. The energy values and essential harmonic character of torsional levels of benzoyl fluoride confirm the earlier supposition[15] that a number of lowest torsional transitions were observed in the far-infrared spectrum[3] as one unresolved band (63.36 $cm^{-1}$). The second spectral band (61.91 $cm^{-1}$) must be assigned to hot transitions of a similar nature.

At last we considered the potential function of internal rotation of nitrobenzene (7), obtained recently,[16] and indicated that the parameter (modulus) of $V_4$ seems to be somewhat overestimated.

The results obtained for benzaldehyde and benzoyl fluoride in this work indicate that the true potential barriers to internal rotation of benzaldehyde and benzoyl fluoride are close to quantum chemical values and not to earlier[1−3] experimental ones.

We can see now that the calculation of the potential barrier to internal rotation for a molecular system comprising a benzene ring with a $\pi$-conjugated substituent (at least such as benzaldehyde and benzoyl fluoride) is not a special problem, and there is no reason more to think about conflict between theory and experiment in this case.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental and calculated geometrical parameters of benzaldehyde molecule, calculated and experimental vibrational frequencies of benzaldehyde, and calculated geometrical parameters of benzoyl fluoride molecule. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: godunov@phys.chem.msu.ru and godunov.msu@gmail.com. Phone: +7 (495) 939 14 69.

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was financially supported by Russian Foundation for Basic Research, Grant No. 13-03-00640a.

## REFERENCES

(1) Miller, F. A.; Fateley, W. G.; Witkowski, R. E. Torsional Frequencies in the Far Infrared — V. Torsions Around the C-C Single Bond in Some Benzaldehydes, Furfural, and Related Compounds. *Spectrochim. Acta, Part A* **1967**, *23*, 891−908.

(2) Kakar, R. K.; Rinehart, E. A.; Quade, C. R.; Kojima, T. Microwave Spectrum of Benzaldehyde. *J. Chem. Phys.* **1970**, *52*, 3803−3813.

(3) Durig, J. R.; Bist, H. D.; Furic, K.; Qiu, J.; Little, T. S. Far Infrared Spectra and Barriers to Internal Rotation of Benzaldehyde, Benzoyl Fluoride, Benzoyl Chloride and Acetophenone. *J. Mol. Struct.* **1985**, *129*, 45−56.

(4) Pitzer, K. S. Energy Levels and Thermodynamic Functions for Molecules with Internal Rotation: II. Unsymmetrical Tops Attached to a Rigid Frame. *J. Chem. Phys.* **1946**, *14*, 239−243.

(5) Coussens, B.; Pierloot, K.; Meier, R. J. Conformations and Rotational Barriers of Aromatic Polyesters: Part II. Rotational Barriers in Parahydroxybenzoic Acid, Polyethylene Terephthalate, and Small Aromatic Moieties. *J. Mol. Struct.: THEOCHEM* **1992**, *259*, 331−344.

(6) Head-Gordon, M.; Pople, J. A. Internal Rotation in Conjugated Molecules: Substituted Ethylenes and Benzenes. *J. Phys. Chem.* **1993**, *97*, 1147−1151.

(7) Meier, R. J. Comment on "Internal Rotation in Conjugated Molecules: Substituted Ethylenes and Benzenes". *J. Phys. Chem.* **1993**, *97*, 10248−10249.

(8) Head-Gordon, M.; Pople, J. A. Reply to Comment on "Internal Rotation in Conjugated Molecules: Substituted Ethylenes and Benzenes". *J. Phys. Chem.* **1993**, *97*, 10250.

(9) Meier, R. J.; Koglin, E. On the Problem of Theoretical Evaluation of the Rotational Barrier in Aromatics with Adjacent Conjugated Group: Benzaldehyde and N-methylbenzamide. *Chem. Phys. Lett.* **2002**, *353*, 239−243.

(10) Speakman, L. D.; Papas, B. N.; Woodcock, H. L.; Schaefer, H. F., III The Microwave and Infrared Spectroscopy of Benzaldehyde: Conflict Between Theory and Experimental Deductions. *J. Chem. Phys.* **2004**, *120*, 4247−4250.

(11) Klug, R. L.; Burcl, R. Rotational Barriers in Azobenzene and Azonaphthalene. *J. Phys. Chem. A* **2010**, *114*, 6401−6407.

(12) Meier, R. J. Comment on "Rotational Barriers in Azobenzene and Azonaphthalene. *J. Phys. Chem. A* **2011**, *115*, 3604.

(13) Burcl, R. Reply to "Comment on 'Rotational Barriers in Azobenzene and Azonaphthalene'. *J. Phys. Chem. A* **2011**, *115*, 3605−3606.

(14) Kakar, R. K. Microwave Spectrum of Benzoyl Fluoride. *J. Chem. Phys.* **1972**, *56*, 1189−1197.

(15) Larsen, N. W.; Pedersen, T.; Sørensen, B. F. Microwave Spectrum and Barrier to Internal Rotation of 4-Fluorobenzoyl Fluoride: Dipole Moments for Benzoyl Fluoride and 4-Fluorobenzoyl Fluoride. *J. Mol. Spectrosc.* **1988**, *128*, 370−383.

(16) Dorofeeva, O. V.; Vishnevskiy, Yu. V.; Vogt, N.; Vogt, J.; Khristenko, L. V.; Krasnoschekov, S. V.; Shishkov, I. F.; Hargittai, I.; Vilkov, L. V. Molecular Structure and Conformation of Nitrobenzene Reinvestigated by Combined Analysis of Gas-Phase Electron Diffraction, Rotational Constants, and Theoretical Calculations. *Struct. Chem.* **2007**, *18*, 739−753.

(17) Werner, H. J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schutz, M.; Celani, P.; Korona, T.; Lindh, R.; Mitrushenkov, A.; Rauhut, G. et al. *MOLPRO*, version 2010.1, a package of *ab initio* programs (see http://molpro.net).

(18) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297−3305.

(19) Abramenkov, A. V. Computational Aspects of Direct and Inverse Spectral Problems for the Model of Hindered Internal Rotation. *Rus J. Phys. Chem.* **1995**, *69*, 948−952.

(20) Lewis, J. D.; Malloy, T. B.; Chao, T. H.; Laane, J. Periodic Potential Functions for Pseudorotation and Internal Rotation. *J. Mol. Struct.* **1972**, *12*, 427−449.

(21) Borisenko, K. B.; Bock, Ch. W.; Hargittai, I. Molecular Geometry of Benzaldehyde and Salicylaldehyde: A Gas-Phase Electron Diffraction and *Ab Initio* Molecular Orbital Investigation. *J. Phys. Chem.* **1996**, *100*, 7426−7434.

(22) Desyatnyk, O.; Pszczółkowski, L.; Thorwirth, S.; Krygowski, T. M.; Kisiel, Z. The Rotational Spectra, Electric Dipole Moments and Molecular Structures of Anisole and Benzaldehyde. *Phys. Chem. Chem. Phys.* **2005**, *7*, 1708−1715.

(23) Silva, C. R.; Reilly, J. P. Theoretical Calculations on the Excited Electronic States of Benzaldehyde and Observation of the $S_2 \leftarrow S_0$ Jet-Cooled Spectrum. *J. Phys. Chem.* **1996**, *100*, 17111−17123.

(24) Green, J. H. S.; Harrison, D. J. Vibrational Spectra of Benzene Derivatives—XXI. Benzoyl Fluoride, Acetophenone, Methyl Benzoate and Related Compounds. *Spectrochim. Acta, Part A* **1977**, *33*, 583−587.

(25) Balfour, W. J. The 280-nm Absorption System of Benzoyl Fluoride. *J. Mol. Spectrosc.* **1980**, *84*, 60−67.

(26) The analogous rotational band contours analysis for benzaldehyde see, for example, in the work by Hollas, J. M.; Gregorek, E.; Goodman, L. Allowed and Forbidden Character in the 3715-Å $\pi^* \leftarrow n$ System of Benzaldehyde. *J. Chem. Phys.* **1968**, *49*, 1745−1753.

(27) Western, C. M. *PGOPHER*, A Program for Simulating Rotational Structure. University of Bristol. http://pgopher.chm.bris.ac.uk.

(28) Bokareva, O. S.; Bataev, V. A.; Godunov, I. A. A Quantum-Chemical Study of the Structure and Conformational Dynamics of the Acrolein Molecule in the Ground Electronic State. *Rus. J. Phys. Chem.* **2009**, *83*, 81−90.

(29) Bokareva, O. S.; Bataev, V. A.; Pupyshev, V. I.; Godunov, I. A. Structure and Dynamics of Acrolein in Lowest Excited $^{1,3}(n\pi^*)$ Electronic States: The Quantum-Chemical Study. *Int. J. Quantum Chem.* **2008**, *108*, 2719−2731.

(30) Correll, T.; Larsen, N. W.; Pedersen, T. Equilibrium Configuration and Barriers of Four Fluorine Substituted Nitrobenzenes, Obtained by Microwave Spectroscopy. *J. Mol. Struct.* **1980**, *65*, 43−49.

(31) Clarkson, J.; Smith, W. E. A DFT Analysis of the Vibrational Spectra of Nitrobenzene. *J. Mol. Struct.* **2003**, *655*, 413−422.