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Cold Snapshot of a Molecular Rotary Motor Captured by High-Resolution Rotational Spectroscopy

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Abstract: We present the first high-resolution rotational spectrum of an artificial molecular rotary motor. By combining chirped-pulse Fourier transform microwave spectroscopy and supersonic expansions, we captured the vibronic ground-state conformation of a second-generation motor based on chiral, overcrowded alkenes. The rotational constants were accurately determined by fitting more than 200 rotational transitions in the 2–4 GHz frequency range. Evidence for dissociation products allowed for the unambiguous identification and characterization of the isolated motor components. Experimental and complementary quantum-chemical calculations provide accurate geometrical parameters for the C20H20 molecular motor, the largest molecule investigated by high-resolution microwave spectroscopy to date.

Inspired by Nature’s ability to perform motor functions at the molecular level, chemists have engaged in the design of synthetic nanomachines that can perform molecular motion in a controlled manner and mimic their biological counterparts using simpler models. An elegant design of a synthetic rotary molecular motor based on chiral, overcrowded alkenes was introduced by Feringa and co-workers. Key features of this design include 1) a light-activated power stroke in which excited-state cis–trans isomerization converts photon energy into mechanical motion and 2) a chiral center that imposes unidirectional motion departing from conventional molecular photoswitching. The operation mechanism of such a motor is illustrated in Figure 1. The system is comprised of a “stator” flanked by an upper “rotor” via a C=C “axle”. An ultraviolet trigger results in photoisomerization of the fluorene unit connected to an upper “rotor” via a C=C “axle”. An ultraviolet trigger results in photoisomerization of the fluorene unit connected to an upper “rotor” via a C=C “axle”. An ultraviolet trigger results in photoisomerization of the fluorene unit connected to an upper “rotor” via a C=C “axle”. An ultraviolet trigger results in photoisomerization of the fluorene unit connected to an upper “rotor” via a C=C “axle".

Figure 1. Structure of the molecular motor. The three components, namely rotor, axle, and stator, are indicated as well as the light-driven (power) and thermal strokes required for operation. Further photon-driven and thermal isomerization events return the motor to its original configuration 1-A.

Figure 1. Structure of the molecular motor. The three components, namely rotor, axle, and stator, are indicated as well as the light-driven (power) and thermal strokes required for operation. Further photon-driven and thermal isomerization events return the motor to its original configuration 1-A.

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phase, on the other hand, is pre-
eminently suited for this purpose
but the largest molecular systems
that have been studied with these
techniques hardly come close to
the molecular motor that is consid-
ered here with respect to the
number of non-hydrogen
atoms\textsuperscript{[11-13]}

Herein, we report on the first
high-resolution rotational spec-
trum of a molecular motor, which
was obtained by combining micro-
wave spectroscopy with the cold
conditions of a supersonic jet.
Microwave spectroscopy enables
the unambiguous identification of
molecular species and the determi-
nation of the thermal distribution
of conformations. Owing to their
unique moments of inertia, each conformation of a particular
molecule can be differentiated by its rotational spectrum.
With the implementation of short and intense microwave
chirps in broadband excitation schemes as in chirped-pulse
Fourier transform microwave (CP-FTMW) spectroscopy, it is
possible to record rotational spectra of complex, flexible
molecules spanning several GHz in a single acquisition\textsuperscript{[14]}

The cold molecular jet brings the molecules to rotational
temperatures below 2 K, which for a molecular system of this
size ($\text{C}_9\text{H}_{30}$, $M_e = 344 \text{ g mol}^{-1}$) implies that the strongest
rotational transitions are situated between 2 and 4 GHz. The
broadband microwave spectrum of 1-A in this region is shown
in Figure 2. The experimental spectrum is shown as the upper
trace (in black). The spectrum shown below (in red)
represents a simulation obtained from the fitted spectroscopic
parameters reported in Table 1. The right panel of this Figure
displays a segment of the rotational spectrum, highlighting
a branch of rotational transitions $J_{a,K_a} \rightarrow J'_{a',K_a'}$ denoted by
the rotational quantum numbers $J, K_a$, and $K_a'$ with $J$ being
the rotational angular momentum quantum number and $K_a$ and
$K_a'$ being the projections of $J$ onto the principal axes at the
prolate and oblate symmetric top limits, respectively. A total of
222 rotational transitions were assigned, and the primary
rotational constants ($A, B, C$) were determined through
a recurrent fit using the A-reduced semirigid rotor Hamilton-
ian as implemented in PGOPHER\textsuperscript{[15]}. Quartic centrifugal
distortion constants ($D_j$ and $d_j$) were also determined. We
note that the inclusion of distortion constants is not required
to achieve a good fit. The small magnitudes obtained for both
$D_j$ and $d_j$ are a strong indicator of the rigidity of the molecule
in spite of its size. A summary of the fitted spectroscopic
parameters is given in Table 1 while a complete list of all fitted
rotational transitions is provided in the Supporting Informa-
tion. We found neither evidence for internal dynamics arising
from the methyl top nor for other large-amplitude motions,
which would point to high barriers associated with these
motions. As the methyl group is part of the ratchet during the
operation of the motor, this is indeed what would be
expected.

In our frequency range, we cover mainly a- and b-type
transitions. In Figure 3, we show segments of the spectrum
depicting a progression of a/b-type quartets over the range
$(J + 1) - J$ of 8-7 to 13-12. Following the progression from
lower to higher frequencies (panels A-F), we observe
a narrowing between transitions, resulting in coalescence
for 13-12 further up the $J$ levels.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
 & Exp. & M06-2X\textsuperscript{[1]} & MP2\textsuperscript{[1]} & B3LYP\textsuperscript{[1]} & B3LYP-D3BJ\textsuperscript{[1]} \\
\hline
$B$ [MHz] & 164.951398(47) & 165.639 & 168.546 & 162.795 & 166.282 \\
$C$ [MHz] & 122.506884(33) & 122.462 & 124.127 & 121.704 & 122.875 \\
\hline
$D_R$ [kHz] & 0.001431(90) & – & – & – & – \\
$D_J$ [kHz] & 3.4 & – & – & – & – \\
\hline
$|J_a|$ [D] & $|y|$ & 1.28 & 1.31 & 1.39 & 1.37 \\
$|J_a'|$ [D] & $|y|$ & 0.99 & 0.55 & 1.03 & 0.99 \\
$|J_c|$ [D] & $|n|$ & 0.12 & 0.05 & 0.15 & 0.11 \\
$N$ & 222 & – & – & – & – \\
$\alpha$ [kHz] & 3.4 & – & – & – & – \\
$\nu$ & $-0.540$ & $-0.536$ & $-0.509$ & $-0.555$ & $-0.532$ \\
\hline
\end{tabular}
\caption{Experimentally determined parameters for the vibronic ground state of the motor identified in the microwave spectrum.\textsuperscript{[a]}}
\end{table}

\textsuperscript{[a]} Rotational constants ($A, B, C$ in MHz) and quartic centrifugal distortion constants (in kHz); type of spectrum observed (a-type, b-type, c-type) with $y$ being observed and $n$ being not observed; predicted dipole moments; number of lines used in the fit; standard error of the fit (in kHz); asymmetry parameter $\kappa = (2B-A-C)/(A-C)$. The experimental frequency accuracy is 25 kHz.\textsuperscript{[b]} 6-311++G** basis set. \textsuperscript{[c]} def2-TZVP basis set.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure2.png}
\caption{Broadband rotational spectrum of 1-A from 2 to 4 GHz (1.5 million averages, measurement time: 13 h). The upper trace (in black) shows the experimental spectrum obtained using neon as the carrier gas. The lower trace represents simulations obtained from the fitted spectroscopic parameters reported in Table 1. The $\dagger$ marks the a/b quartet progressions that are shown in detail in Figure 3. The rotational transition marked with $^\dagger$ corresponds to the dissociation structure of the rotor as a consequence of fragmentation (see main text). The spectroscopic parameters of the fragment are reported in Table 2.}
\end{figure}
The characteristic a/b transitions from the crystal structure of the fragment are marked with red in Figure 2. The spectroscopic parameters obtained from the fit to these transitions are given in Table 2. Quantum-chemical calculations on two tentative structures, with the values obtained from the crystal structure, shows that the equilibrium ones.

Interestingly, we also found evidence that under our experimental conditions, some fragmentation of the molecular motor occurs. In the rotational spectrum, we identified and fitted a series of rotational lines that correspond to dissociation products of the rotor and the stator. Fragmentation occurs owing to preexpansion heating at the nozzle. One of the 23 rotational transitions belonging to the rotor moiety is shown in Figure 2 (right panel). The spectroscopic parameters obtained from the fit to these transitions are given in Table 2. Quantum-chemical calculations on two tentative structures of the rotor confirmed our expectations: from the comparison of rotational constants, dipole moment components, and asymmetry parameters, we unambiguously identified r-B as the structure of the fragment. Dissociation thus results in a planar rotor fragment that no longer possesses a chiral center as compared with the geometry of the rotor when it is coupled to the motor. The stator fragment was unambiguously assigned to fluorene based on a fit using 18 rotational transitions and a direct comparison with reported rotational constants.

In summary, we have presented the first high-resolution rotational spectrum of a molecular rotary motor and used it to determine the exact conformation of the motor in its vibronic ground state and to derive key structural parameters. Rotational constants were determined with high accuracy and provide an excellent basis for benchmarking the current levels of theory implemented in quantum-chemical methods for large molecular systems. Temperature-induced fragmentation around the axle, we defined three planes (Figure 4), which comprise the planar part of the stator (in yellow), the axle and rotor (in blue), and the planar part of the rotor (in red), respectively. The angles $\alpha = 50.8^\circ$ ($50.0^\circ$), $\beta = 42.0^\circ$ ($39.6^\circ$), and $\gamma = 18.4^\circ$ ($22.8^\circ$) define the relative twisting of the rotor with respect to the stator in the locked conformation (crystal structure values are given in parentheses). Comparison with the values obtained from the crystal structure shows that the structure of the motor is unmistakably affected by its environment. The gas-phase dihedral angle at the axle coordinate differs by approximately 1.6° from the crystal structure, with $D(2-3-4-5) = 13.5^\circ$ ($15.18^\circ$).

In Table 1, we compare the results taken from our observations with a series of quantum-chemical calculations at different levels of theory (see the Supporting Information for further details). We found a very good agreement between theoretical predictions and our experimental observations at all levels of theory. The most impressive match between the experimental and calculated rotational constants was obtained at the M06-2X/6-311+G** level of theory, for which experiment and theory differ by less than 0.5% for all three rotational constants. In addition, the magnitudes of the permanent dipole moment components are in good agreement with the observed intensities. At the same time, the dispersion-corrected B3LYP-D3BJ level of theory predicts the experimental rotational constants equally well, in particular if one considers the deviations (ca. 1%) predicted for vibrationally corrected rotational constants with respect to the equilibrium ones.

The excellent agreement between experiment and theory enabled us to determine key geometrical parameters of the molecular motor. The length of the C–C bond of the motor is 1.356 Å (M06-2X), which is very similar to the length determined from the crystal structure (1.357 Å). Comparison of this bond length with those of other non-sterically overcrowded alkenes, such as ethylene (C2H4, 1.325 Å) and 2-butene (C4H8, 1.329 Å), readily indicates that the C–C bond is substantially extended in the molecular motor. To evaluate the local geometry of the rotor (1-A) obtained at the M06-2X/6-311+G** level of theory. Relevant geometrical parameters are given; the C–C bond length is 1.356 Å (the value in parentheses refers to the length taken from the crystal structure), the depicted planes with respect to the respective numbered atoms (yellow: 1-2-3; blue: 3-4-5; red: 5-6-7) define the local torsions around the axle. The angles between the planes are $\alpha = 50.8^\circ$, $\beta = 42.0^\circ$, and $\gamma = 18.4^\circ$. The dihedral angle $D(2-3-4-5)$ is 13.5° (M06-2X/13.8° (B3LYP-D3BJ)).
Table 2: Experimental and calculated spectroscopic parameters of the rotor fragment.\(^{[a]}\)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Exp.</th>
<th>(r\text{-A}^{\text{H}})</th>
<th>(r\text{-B}^{\text{H}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A \text{ [MHz]})</td>
<td>1591.057(12)</td>
<td>1469.574</td>
<td>1598.998</td>
</tr>
<tr>
<td>(B \text{ [MHz]})</td>
<td>488.12288(21)</td>
<td>515.633</td>
<td>489.503</td>
</tr>
<tr>
<td>(C \text{ [MHz]})</td>
<td>375.37307(20)</td>
<td>408.807</td>
<td>376.200</td>
</tr>
<tr>
<td>(</td>
<td>\alpha_{a}</td>
<td>\text{ [D]})</td>
<td>6</td>
</tr>
<tr>
<td>(</td>
<td>\alpha_{b}</td>
<td>\text{ [D]})</td>
<td>7</td>
</tr>
<tr>
<td>(</td>
<td>\alpha_{c}</td>
<td>\text{ [D]})</td>
<td>8</td>
</tr>
<tr>
<td>(N)</td>
<td>23</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>(\sigma \text{ [kHz]})</td>
<td>3.9</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>(\kappa)</td>
<td>–0.81</td>
<td>–0.79</td>
<td>–0.81</td>
</tr>
</tbody>
</table>

[a] Rotational constants \((A, B, C \text{ in MHz})\); type of spectrum observed \((a\text{-type, b\text{-type, c\text{-type}}})\) with \(y\) being observed and \(n\) being not observed; predicted dipole moments; number of lines used in the fit; standard error of the fit \((\text{in kHz})\); asymmetry parameter \(\kappa = (2B-A-C)/(A-C)\). The experimental frequency accuracy is 25 kHz. [b] M06-2X/6-311++G***.

of the motor has allowed us to observe the motor components separately and analyze the structures of the dissociation products. The unprecedented observation of a molecule of this size by microwave spectroscopy introduces exciting perspectives to the investigation of other molecules of similar and larger sizes by high-resolution spectroscopy. In the present study, we have reported on the conformation of the motor in the absence of an external trigger and observed a single conformer corresponding to the thermally stable ground-state structure. These studies served to demonstrate the feasibility of high-resolution rotational spectroscopic studies on systems of this size. Experiments that have now come within reach use UV photons to drive the initial power stroke of the motor and combine this activation of the motor with the high resolving power of rotational spectroscopy to determine the structure of intermediate metastable mechanical steps in the photocycle of these molecular machines. Such experiments are presently being set up in our laboratories.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: high-resolution spectroscopy · large molecules · microwave spectroscopy · molecular motors · structure elucidation

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