



Contents lists available at ScienceDirect

Tetrahedron

journal homepage: [www.elsevier.com/locate/tet](http://www.elsevier.com/locate/tet)

## High-resolution gas-phase spectroscopy of a single-bond axle rotary motor

Elena Maltseva<sup>a</sup>, Saeed Amirjalayer<sup>b, c</sup>, Arjen Cossen<sup>d</sup>, Wesley R. Browne<sup>d</sup>,  
Ben L. Feringa<sup>d</sup>, Wybren Jan Buma<sup>a, \*</sup>

<sup>a</sup> University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

<sup>b</sup> Physikalisches Institut, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Strasse 10, 48149 Münster, Germany

<sup>c</sup> Center for Nanotechnology, Heisenbergstrasse 11, 48149 Münster, Germany

<sup>d</sup> Stratingh Institute for Chemistry and Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

### ARTICLE INFO

#### Article history:

Received 2 April 2017

Received in revised form

17 May 2017

Accepted 18 May 2017

Available online xxx

#### Keywords:

Overcrowded alkene-based molecular motor  
Electronic structure  
Molecular beam spectroscopy  
DFT computational studies  
Resonant two-photon ionization

### ABSTRACT

High-resolution laser spectroscopy in combination with molecular beams and mass-spectrometry has been applied to study samples of a prototypical rotary motor. Vibrationally well-resolved excitation spectra have been recorded that are assigned, however, to a structural isomer of the original rotary motor which is formed in situ under the elevated temperatures required experimentally. In this isomer the 'rotor' and 'stator' parts are to a large extent conjugationally disconnected leading to excited-state properties that are dominantly determined by the 'rotor' with the 'stator' acting as observer.

© 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

### 1. Introduction

Inspired by nature, current technology is increasingly aiming for motion that can be controlled at the molecular level. Artificial molecular machines thus nowadays attract tremendous interest as they offer the potential for such a control. Although in many aspects still in its infancy, the field has in recent years matured quickly leading to applications that range from light-controlled catalysis<sup>1–4</sup> to functionalization of surfaces<sup>5,6</sup> and various nanotools in medicine.<sup>7–10</sup>

Rotary motors based on overcrowded alkenes have in this respect shown to be particularly attractive because their properties can be tuned and controlled relatively easily and because light can be used to address them in a non-invasive manner.<sup>11–14</sup> Such rotary motors consist of a 'rotor' and 'stator' part that are linked by a double bond 'axle'. Activation of these motors occurs by photoexcitation which initiates a cis-trans isomerization of the 'axle'. Since

this step effectively provides the 'power stroke' for the further mechanical motion, it has attracted considerable attention from both experimentalists<sup>15,16</sup> and theoreticians.<sup>17–19</sup> Femtosecond time-resolved fluorescence studies on **1** (Fig. 1) have found that photoexcitation of the motor is followed by ultrafast (100 fs) relaxation from the Franck-Condon region of the electronically excited 'bright' state to a 'dark' state that decays on a ps time scale.<sup>11</sup> In these studies it was put forward that this 'dark' state is associated with a region of the potential energy surface of the 'bright' state with a low oscillator strength, a suggestion that was later supported by computational studies.<sup>20</sup>

Such a two-state isomerization mechanism could, however, not be reconciled with data obtained in subsequent femtosecond time-resolved IR absorption studies on the same system.<sup>21</sup> These studies indicated that the initially excited 'bright' state undergoes an ultrafast internal conversion process to a different electronically excited 'dark' state that for vertical excitation is quasi-degenerate with the 'bright' state but crosses it when the molecule starts to structurally relax on the potential energy surface of the 'bright' state. Calculations predict that in this 'dark' state the molecule has to overcome a barrier to access the conical intersection with the

\* Corresponding author.

E-mail address: [W.J.Buma@uva.nl](mailto:W.J.Buma@uva.nl) (W.J. Buma).

<http://dx.doi.org/10.1016/j.tet.2017.05.064>

0040-4020/© 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

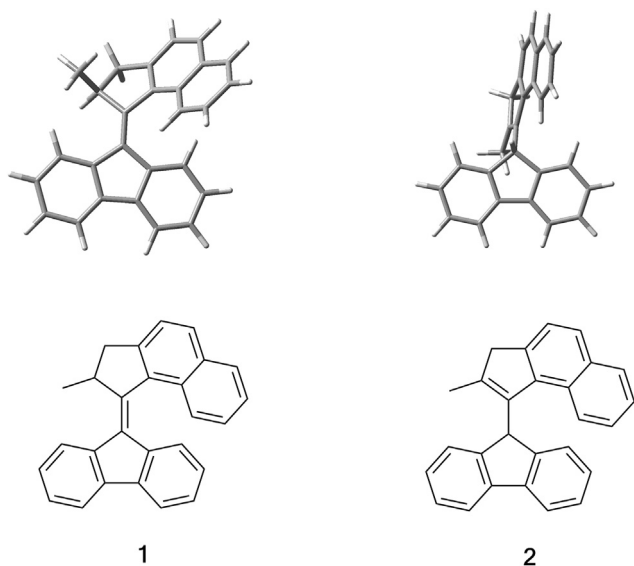


Fig. 1. Chemical structure of molecular rotor **1** and its isomer **2**.

ground state that leads to isomerization. This three-state model found further support in CASSCF and CASPT2 calculations - the most advanced calculations possible at this moment for such molecular motors - on a slightly smaller rotary motor.<sup>17</sup>

In view of the above it is clear that a further characterization and understanding of the potential energy surfaces of the lower electronically excited states of **1** is of considerable interest. Ideally, such studies would be performed under conditions in which the molecule is isolated and not affected by its environment. Normally, one would tend to think that such studies need a time-domain approach using femtosecond laser spectroscopic techniques. However, we have shown recently in nanosecond laser spectroscopic studies on the isomerization mechanism of isolated trans-azobenzene<sup>22</sup> that frequency-domain studies can provide a direct - and in some aspects even more detailed - view on the photophysics and photochemistry of electronically excited states with lifetimes down to 170 fs. In the present studies we therefore aimed to apply these high-resolution nanosecond techniques together with supersonic molecular beams and mass-spectrometry on samples of **1** in order to perform mass-selective vibrationally-resolved spectroscopy of this rotary motor. It will be shown that such spectra can indeed be recorded, but further consideration of the observed spectroscopic properties and excited-state dynamics lead to the conclusion that these spectra must be assigned to an isomer of **1** in which 'rotor' and 'stator' are only connected by a single-bond 'axle' (isomer **2**, Fig. 1).

## 2. Results and discussion

Fig. 2a displays the  $(1 + 1')$  RE2PI excitation spectrum of the sample detected at  $m/e = 344$  a.m.u., the mass of the molecular ion, and recorded in the  $28500\text{--}30800\text{ cm}^{-1}$  (351–325 nm) frequency region. The spectrum shows well-separated bands with a line width between  $1.1$  and  $1.5\text{ cm}^{-1}$ . Outside this region no other bands have been detected. The lowest-energy band in this spectrum occurs at  $28618.8\text{ cm}^{-1}$ . Since at lower excitation energies no other bands are observed we assign this band as the 0-0 transition to the lowest electronically excited state. Interestingly, the vibronic activity in this spectrum is rather limited: apart from the strong 0-0 transition only a few low-intensity bands are present at higher excitation energies (Fig. 2a). Quantum chemical calculations on **1**

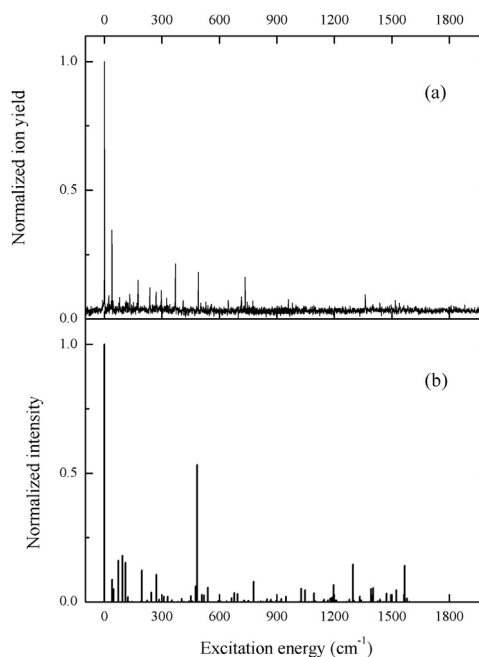


Fig. 2. (a):  $(1 + 1')$  RE2PI excitation spectrum taken at molecular mass of molecular rotor; (b)  $S_1 \leftarrow S_0$  simulated fundamental excitation spectrum of **2** excluding modes at 20 and  $85\text{ cm}^{-1}$ . Excitation energies are given with respect to the 0-0 transition at  $28618.8\text{ cm}^{-1}$ .

predict that for vertical excitation the lower two electronically excited states are quasi degenerate.<sup>21</sup> One of these two states has a large oscillator strength, while the other one has an oscillator strength that is three orders of magnitude smaller. Importantly, these calculations do not find a stable energy minimum on the potential energy surface of the 'bright' state, but for the 'dark' state such a minimum is found without problem. One would thus in first instance be inclined to assign the excitation spectrum to the excitation spectrum of the 'dark' state.

The wavelength at which the 0-0 transition is detected ( $349.4\text{ nm}$ ) is in that case, however, quite puzzling since the absorption spectrum of **1** dissolved in cyclohexane shows a band associated with absorption by the 'bright' state that has a maximum at  $390\text{ nm}$  and extends to  $440\text{ nm}$ .<sup>21</sup> Assignment of the spectrum in Fig. 2a to the 'dark' state would imply that the 'bright' state is at shorter wavelengths than  $\sim 350\text{ nm}$ . Although a blue shift of the absorption spectrum upon going from solution to the gas phase is quite normal, the magnitude of the shift observed here falls outside the range one would expect. A scenario that theoretically might lead to such a large shift is that the molecule adopts a significantly different geometry - in particular with respect to the dihedral angle between the rotor and the stator part - under solution and gas-phase conditions. However, such an explanation is not supported by recent high-resolution rotational spectroscopic experiments on **1**<sup>23</sup> which for all practical purposes show that in the gas phase the 'rotor' and 'stator' adopt the same relative orientation as determined previously with X-ray crystallography.<sup>24</sup>

For the further assignment of the excitation spectrum in Fig. 2 it is instructive to consider the absorption spectra of the isolated stator and rotor moieties. The 'stator' is then a simple fluorene entity that has its absorption maximum around  $300\text{ nm}$ <sup>25</sup> in solution and its 0-0 transition at  $296.0\text{ nm}$  in supersonic expansions.<sup>26</sup> The 'rotor' part, on the other hand, is an alkyl-substituted naphthalene with an absorption maximum around  $315\text{--}320\text{ nm}$ .<sup>27</sup> In the rotary motor an extended conjugated system

Download English Version:

<https://daneshyari.com/en/article/5212173>

Download Persian Version:

<https://daneshyari.com/article/5212173>

[Daneshyari.com](https://daneshyari.com)