Mapping the Excited-State Potential Energy Surface of a Photomolecular Motor

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Abstract: A detailed understanding of the operation and efficiency of unidirectional photomolecular rotary motors is essential for their effective exploitation in molecular nanomachines. Unidirectional motion relies on light-driven conversion from a stable (1a) to a metastable (1b) conformation, which then relaxes through a thermally driven helix inversion in the ground state. The excited-state surface has thus far only been experimentally characterised for 1a. Here we probe the metastable, 1b, excited state, utilising ultrafast transient absorption and femtosecond stimulated Raman spectroscopy. These reveal that the “dark” excited-state intermediate between 1a and 1b has a different lifetime and structure depending on the initial ground-state conformation excited. This suggests that the reaction coordinate connecting 1a to 1b differs to that for the reverse photochemical process. The result is contrasted with earlier calculations.

Light-driven molecular motors based on the chiral overcrowded alkene motif convert the energy of incident photons into intramolecular rotational motion.[1] As such they have the potential to act as a power source for the molecular machines of the future.[2] The essential operational features of light-driven molecular rotary motors are illustrated in Figure 1.[3] The lowest-energy ground-state conformation (1a) comprises a “stator” linked through a double bonded “axle” connected to a “rotor”, which has a stereogenic centre. The molecule is nonplanar due to steric strain. Excitation of the lowest-energy π-to-π* transition localised on the axle reduces the bond order, releasing steric strain and hence a barrierless structural relaxation. The result of this excited-state structure change is isomerization leading ultimately to population of the metastable ground state 1b with a yield of 5–20% depending on the substituents.[4] The conformation 1b can then relax to 1a by a ground-state thermal isomerization either in the reverse or the forward direction, but the forward helix inversion step is overwhelmingly favored due to a lower energy barrier, leading to a half rotation and, for the symmetrical motors studied here, population of 1a but rotated by 180° (Figure 1). Absorption of a second photon followed by a second forward helix inversion completes one cycle of rotor motion. Optimization of the molecular structure has led to motors of the general structure 1a with rotation rates in the MHz frequency range.[3b] Recent synthetic advances demonstrated cooperative rotation of two coupled motors.[5] Although progress has been rapid, many challenges remain before such motors form components of functioning molecular machines, including: more detailed understanding of the structure change accompanying excited-state reaction; understanding how structure change couples to molecular environment; knowledge and control of the photochemical quantum yield. Each of these requires an accurate picture of the excited-state potential energy surface (PES) and its coupling to the ground state.

Previously we characterized the excited-state dynamics of 1a by ultrafast Time-Resolved Fluorescence (TRF), Transient
Absorption (TA) and Femtosecond Stimulated Raman Spectroscopy (FSRS). The initial Franck–Condon (FC) excited state was observed to relax in 100 fs to a “dark” (i.e. with negligible transition moment to \(S_0\)) state which undergoes fast intramolecular vibrational cooling and picosecond excited-state relaxation, leading to formation of a vibrationally hot \(1b\) ground state. Similar measurements using transient IR spectroscopy were reported in a joint theoretical and experimental study. These studies of \(1a\) excited-state dynamics stimulated high quality quantum chemical calculations. Three recent examples point to a reaction coordinate that involves both pyramidalization at the fluorenyl–axle carbon (C9) and torsional motion about the axle; consistent with the observed solvent friction dependence. These calculations reveal the fundamentally multidimensional nature of the reaction coordinate (in contrast to the 1D Figure 1). Torsion and pyramidalization coordinates comprise a basin-like excited-state PES with the dark-state minimum around which FC\(1a\), FC\(1b\) and two conical intersections (CIs) are located. Here we probe experimentally the pathway from FC\(1b\) and contrast it with \(1a\) excitation. However, the calculations are not entirely self-consistent. Two suggest that dynamics involve a crossing of two excited states, while two others find that the dynamics occur on a single PES. Furthermore, two have investigated the entire \(1a/1b\) PES in both ground and excited states, which has not yet been characterized experimentally. Kazaryan et al. calculated excited-state decay dynamics following both \(1a\) and \(1b\) excitation, reporting an overall slower decay for \(1b\), while Pang et al. made a detailed simulation of excited-state dynamics following \(1b\) excitation, but did not track the pathway for \(1a\) excitation.

Here we present the first detailed experimental study of excited-state dynamics following excitation of the metastable \(1b\) form, and contrast them with data for \(1a\). We follow the population dynamics using TA and probe dark-state structures with FSRS; transitions and structural dynamics probed are indicated in Figure 1. Remarkable differences are found between \(1a\) and \(1b\) excited-state structures and dynamics, suggesting distinct relaxation pathways; these data are not in complete agreement with recent calculations, and thus present a future challenge to theory.

Figure 2A shows the measured absorption spectra for \(1a\) and for the photostationary state (\(1a + 1b\)) obtained on continuous irradiation at 385 nm, along with the absorption spectrum of \(1b\) calculated from them (see section S1 in the Supporting Information). The solvent is cyclohexane. As previously described \(1b\) is red-shifted with respect to \(1a\). Excitation at 450 nm exclusively pumps the \(S_0\) \(\rightarrow\) \(S_1\) transition of \(1b\). Figure 2B shows the TA spectrum for \(1b\) recorded 100 fs after excitation at 450 nm by 100 fs pulses; it is contrasted with the same spectrum for \(1a\) excited at 405 nm (which matches that reported for 390 nm excitation). The time-dependent TA spectra of \(1b\) are shown for completeness (Figure S1). The two TA spectra are similar but there are significant differences. Both show two transitions, the lower energy transition (ca. 740 nm) is ascribed to the FC state, which decays rapidly (ca. 100 fs) to an equilibrium between it and a dark state, which absorbs near 520 nm. These two transitions are slightly blue-shifted compared to the TA spectra of \(1a\). The dark-state spectrum formed following \(1b\) excitation also has a steeper profile on the blue edge than observed for \(1a\), which reflects the negative contribution below 500 nm arising from the ground-state bleach (the bleach recovery dynamics are shown in Figure S2). A much more remarkable difference becomes apparent from the comparison of the time dependences (Figure 2C). The dark state formed on \(1a\) excitation was previously shown to act as the precursor to formation of the (vibrationally hot) \(1b\) product with a lifetime of 1.6 ps. A dark state with a similar spectrum is formed following excitation of \(1b\) (Figure 2B), but its decay is markedly accelerated, by a factor of approximately 7 (Figure 2C) compared to that of \(1a\).

The observation of an accelerated decay for the dark state populated on \(1b\) excitation is significant, as it shows again that the one-dimensional potential surface imagined in Figure 1 is too simple—the dark states reached following excitation of \(1a\) and \(1b\) are not the same, or at least have significantly different
relaxation rates. We note that this finding correlates with the experimental report of a 1:3.5 ratio of forward/reverse quantum yields.[5] Furthermore, the calculations of Kazaryan et al. reported a difference in yield following excitation of 1a and 1b (albeit for a motor of significantly different structure to that studied here). However, in that case the 1b excited state was calculated to be longer lived than 1a, which differs from the present result (Figure 2C).[6]

Whether the dark states reached by excitation of the different ground states have different structures as well as decay rates is important, and can in principle be resolved by transient vibrational spectroscopy. We recently showed that FSRS reveals details of the relaxation in 1a from the FC state to the dark state and onwards to 1b.[6d] It is thus interesting to compare the structures of the dark states reached by the different excitation routes. Unfortunately, the rapid decay which dominates the early part of the relaxation of the dark state formed from 1b (Figure 2C) means that the FSRS would be measured in the region of pulse overlap, which leads to contributions from “coherent artefacts” which can distort FSRS data. To obtain high-quality spectra for the dark state we exploit the earlier observation that the introduction of a cyano substituent at the S’ position on the naphthyl rotor (1a-CN, Figure S10) results in an extended lifetime for the dark state, arising from a modification to the excited-state surface, but yields otherwise similar behavior to 1a.[4] We repeated the TA measurements for 1a-CN and 1b-CN, and recovered qualitatively the same results as for 1a/1b: TA are blue-shifted for excitation of 1b-CN, and the lifetime of the dark state is significantly shortened, in this case from approximately 10 ps to 3 ps, with the decay of 1a-CN being well represented by single exponential kinetics, while the faster 1b-CN decay departs slightly from single exponential behavior, a result which may reflect incomplete vibrational cooling following the 100 fs FC state decay[4,6b] (Figure 3A,B; corresponding time dependent TA and fits are shown in Figures S3–S6).

The longer lifetime of the dark state facilitates time resolved FSRS, and data for 1a-CN and 1b-CN are contrasted in Figure 3C, and shown as a function of time in Figure 3D. Figure 3C compares the Raman spectra of dark states reached through 1a-CN and 1b-CN (averaged between 200 and 500 fs to improve signal-to-noise—the full temporal evolution is shown in Figures 3D and S7). The FSRS spectra differ in two respects. First, in the higher wavenumber region (> 1000 cm⁻¹) the most intense peak is at 1460 cm⁻¹ in 1b-CN but red-shifted to 1350 cm⁻¹ in 1a-CN. There are other smaller differences in this region, with the most intense FSRS peak for 1b-CN being broader than for 1a-CN. In the lower frequency region there is a second major difference with the mode at 350 cm⁻¹ for 1a-CN absent or strongly shifted for 1b-CN. These differences point to distinct structures for the two dark states reached from different ground states. Aside from these notable differences there is overlap between the two FSRS, with many modes showing the same or similar frequencies and amplitudes (as expected, since they are localized on the two aromatic rings and therefore less likely to be involved in the reaction coordinate, and thus modified on dark-state formation[6b]).

Although the observed differences in FSRS point to distinct structures, the assignment of the spectral changes is less straightforward. This is partly because the calculations which aided assignment of ground-state vibrational modes[6b] are less readily obtained for excited electronic states of large molecules on reactive potential surfaces. For 1a the FSRS data were discussed earlier[6b] In the ground state there are a few intense Raman active modes mainly involving C=C stretches of the “axle”. The excited-state spectrum is much
more complex, and overall shifted to lower wavenumber. The shift to lower wavenumber can be assigned to a reduced bond order on the “axle”. The increased complexity was previously ascribed to the different resonances (S₁→S₀ and S₁→S₄) on which the spectra are generated, leading to different enhancement patterns.⁶⁶ These arguments apply to 1b-CN, where increased complexity and an overall red shift compared to the ground state are also observed (Figure S7,8). It is the complexity of the S₁ spectra that prohibits a direct assignment of the blue shift observed between 1a-CN and 1b-CN (Figure 3C) to a specific structural change, for example, to a shortening of the “axle” C=–C bond in the 1b-CN dark state; this could be investigated through quantum chemical calculations.

A second potential contribution to the spectral changes in Figure 3C is different resonance conditions for 1a-CN and 1b-CN. It has been shown experimentally and in theory that FSRS spectra may depend on the resonance wavelength.⁶⁷ To check for this we recorded FSRS for 1a-CN at wavelengths across the transient spectrum. At least on the Stokes side of the S₁→S₀ dark-state transition (where all present FSRS measurements were made) the spectra are only a weak function of Raman wavelength, and do not reproduce the changes observed between 1a-CN and 1b-CN (Figure S9). Thus, the structure change between dark states detected in FSRS is real, although, in the absence of accurate excited-state calculations of vibrational spectra, structural assignment is elusive.

The time dependence (Figure 3D) shows no temporal evolution in the FSRS spectrum of 1b-CN dark state during its lifetime, suggesting that thermalization of the vibrationally hot dark state formed in 100 fs from the FC state is essentially complete on the timescale of its 3 ps lifetime, consistent with the near exponential decay observed (Figure S6). The hot ground state formed as the dark-state decays is detected at 1560 cm⁻¹ and itself decays in tens of picoseconds as the ground state cools. This is as previously observed for 1a⁶⁸ but for both 1a-CN and 1b-CN the ground-state signal is much weaker, as the Raman pump wavelength is further from resonance with the S₀ absorption.

The present results establish that excitation of the metastable 1b molecular rotor is followed by ultrafast decay of the FC state to a dark state with a markedly reduced lifetime and distinct structure, compared to that accessed from the thermodynamically favored 1a state. Thus, either the dark state reached following 1a or 1b excitation is not common to the two ground states, or the way in which it is prepared results in the different lifetimes observed, for example by accessing different CIs for internal conversion to the ground state. These results can be discussed in the context of the two calculations which included the 1b excited-state surface. Pang et al. found that the S₁ surface had a single minimum, independent of the initial geometry.⁶⁹ If that were the case then the observed difference in lifetime for that common state must reflect dynamical effects, that is, the pathway from the different initial geometries, rather than the final state reached. This is conceivable for 1a/b, as the initial decay of the dark state reached through 1b is very fast (ca. 200 fs, Figure 2C) and may not be thermalized during its lifetime. However, the lifetime for 1b-CN is 3 ps, which is adequate for thermalization, so the different decay times observed suggests distinct minima. Different minima in-turn suggest different structures, consistent with the vibrational spectra observed (Figure 3C). Kazaryan et al. presented calculations for a somewhat different motor to that studied here (and by Pang et al.), and found distinct minima on S₁ associated with the 1a and 1b states; this is consistent with the present observations.⁷⁰ However, the lifetimes on the excited-state surface were calculated to be slightly longer for the 1b than the 1a-like form, which is the opposite to our observations (albeit for a different molecule) (Figure 2C,B). The dark-state decay time will depend sensitively on the relative locations and energies of the dark-state minima and the CIs with the ground states, so high level quantum mechanical calculations will be required to reproduce the present data, and even then medium effects might introduce significant differences. These results further suggest that the different motor structures may exhibit significant differences in excited-state dynamics; further work is in progress on this.

In summary, the excited-state structure and dynamics for the metastable state of a molecular rotor have been measured for the first time, and contrasted with data for the stable form. Both states decay to intermediate dark states on an ultrafast (ca. 100 fs) timescale, but the dark states attained have distinct structures and lifetimes. Neither feature was predicted by calculations. Thus, these data should stimulate further theoretical investigations of excited-state dynamics which, together with further experiments, will provide an accurate and detailed view of the excited-state potentials of molecular rotors.

**Experimental Section**

The methods and conditions for TA, FSRS and data analysis are described in detail in section S12 in the Supporting Information and elsewhere.⁶⁸ The FSRS data were measured as Raman gain on the low-energy side of the Raman pump wavelength. The synthesis and characterization of 1a and 1a-CN were presented previously.⁹

**Acknowledgements**

S.R.M. is grateful to EPSRC for financial support (EP/J009148/01, EP/N033647/1). B.L.F gratefully acknowledge generous support from NanoNed, the Netherlands Organization for Scientific Research (NWO-CW Top grant to BLF), the Royal Netherlands Academy of Arts and Sciences (KNAW), the Ministry of Education, Culture and Science (Gravitation program 024.001.035) and the European Research Council (Advanced Investigator grant number 694345 to BLF).

**Conflict of interest**

The authors declare no conflict of interest.
Keywords: energy conversion · excited states · molecular motors · photochemistry · ultrafast dynamics

How to cite: Angew. Chem. Int. Ed. 2018, 57, 6203–6207
Angew. Chem. 2018, 130, 6311–6315


Manuscript received: February 16, 2018
Accepted manuscript online: April 6, 2018
Version of record online: April 2018, 27