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Ultrafast Vibrational Cooling Inside of a Molecular Container

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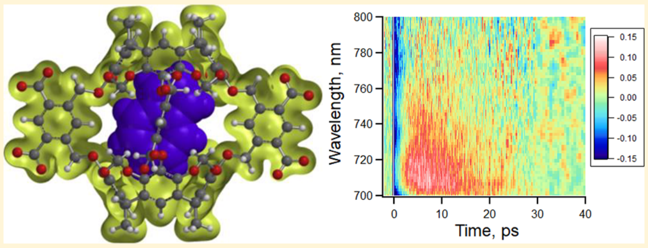
Supporting Information

ABSTRACT: Vibrational cooling of azulene encapsulated in a hemicarcerand molecular container was studied by pump−probe spectroscopy. Within 1.5 ps of excitation of azulene to the S_1 state, rapid internal conversion through a conical intersection leads to the formation of a vibrationally hot (∼1080 K) ground state, the subsequent cooling of which can be monitored by tracking the evolution of the red-shifted hot band at the edge of the ground-state absorption. It was found that the cooling of the hot S_0 state of azulene in the host−guest complex (hemicarceplex) is 2−4 times faster than that in common organic solvents. Such large acceleration points to a high density of matching vibrational modes and efficient mechanical coupling between the guest and the host. The experimental observations were fully corroborated by the results of molecular dynamics simulations.



Vibrationally hot molecules are at the center of many chemical processes, from combustion to photoinduced reactions.[1] Conversion of light into heat and dissipation of thermal energy are of paramount importance in photochemistry. These processes often determine the photostability of the compounds, as well as influence the rates and the yields of photoinduced reactions. It is remarkable that small organic molecules can reach vibrational temperatures as high as a few thousand Kelvin upon excitation with a single photon.[2,3] Such extreme temperatures and local temperature gradients cannot be obtained in solution by any bulk heating methods. In this Letter, we turn our attention to vibrational cooling (VC) of azulene encapsulated in a hemicarcerand[4] host (Figure 1a). Confinement inside of a molecular container has been demonstrated to have a dramatic effect on chemical reactions[5−10] as well as photoinduced electron[11−14] and electronic energy transfer[15−19] mediated by the walls of the cage. In contrast, the influence of host−guest complex formation on the vibrational relaxation and thermal equilibration of the guest molecule remains largely unexplored, despite the fact that cooling dynamics should be significantly affected by such a unique environment.

It is important to emphasize that the formation of vibrationally hot ground states is not a rare phenomenon restricted to a handful of molecules. On the contrary, it is universal and occurs in any species undergoing internal conversion (IC) or intersystem crossing (ISC), regardless of how fast or slow the bulk kinetics is and for what fraction of the excited-state decay it accounts. In all IC and ISC events, excess energy equivalent to at least the $\upsilon = 0$ energy of the electronic excited state is converted into intramolecular vibrations of the ground state. For example, 70−80% of the population of the relatively long-lived ($\tau \approx 30$ ns) S_1 state of benzene decays via IC and results in a hot ground state with an internal temperature in excess of 3000 K. Because processes such as charge transfer or isomerization often occur on a similar picosecond time scale as VC, they are likely to be strongly influenced by such large departures from thermal equilibrium. Understanding of the mechanisms underlying vibrational relaxation is essential if one would like to control the outcome of photochemical reactions.[20]

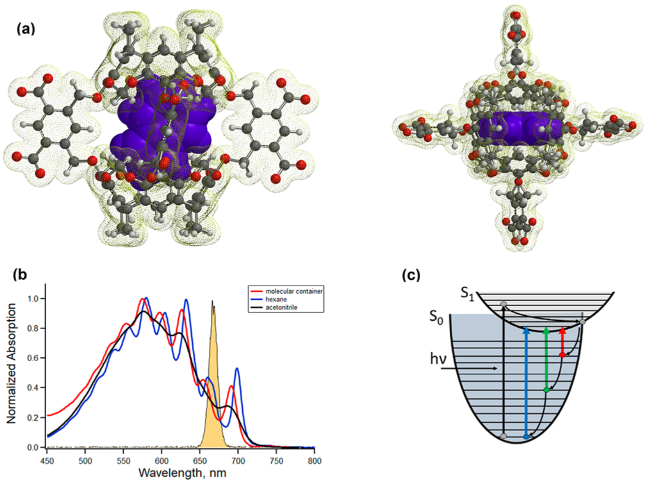


Figure 1. (a) Optimized space-filled structure of the hemicarceplex (Spartan'14, PM6),[26] (b) ground-state absorption spectra of azulene in the hemicarcerand (red), in hexane (blue), and in acetonitrile (black); the spectrum of the pump laser pulse is shown in yellow; (c) energy diagram of VC in azulene illustrating the red shift of the absorption: hot ground state (red and green) vs relaxed ground state (blue).

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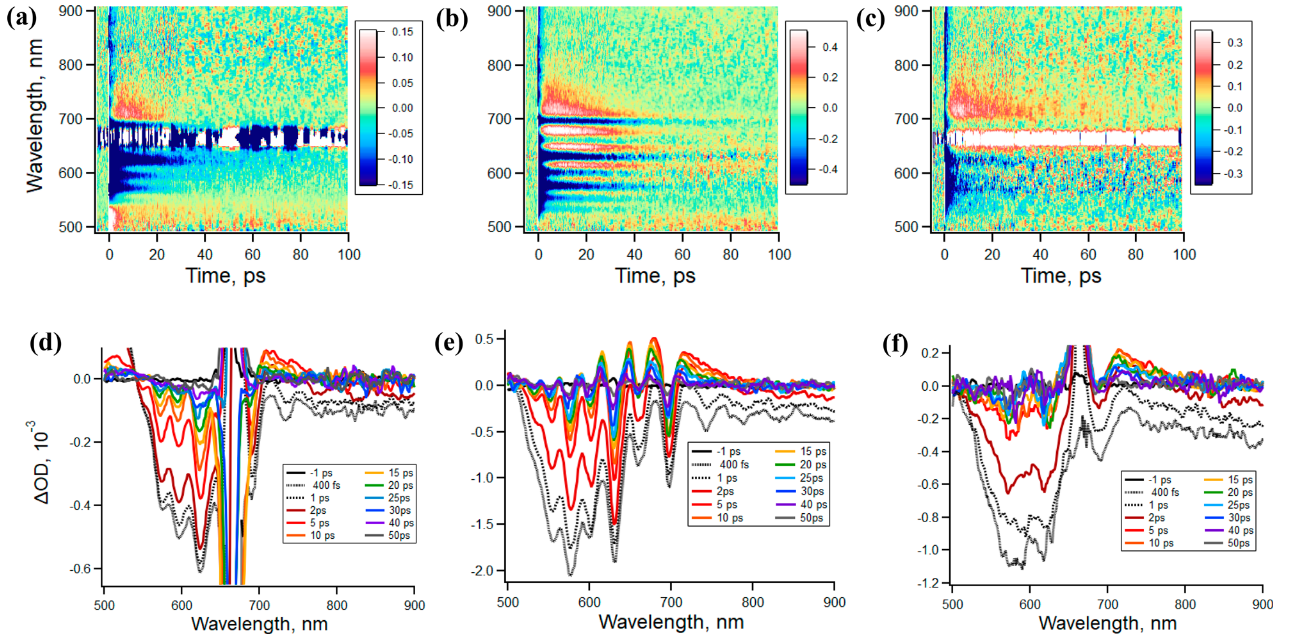

Figure 2. Transient absorption maps for azulene in (a) the hemicarcerand, (b) hexane, and (c) acetonitrile. Transient absorption spectra measured at different delays for azulene in (d) hemicarcerand, (e) hexane, and (f) acetonitrile.

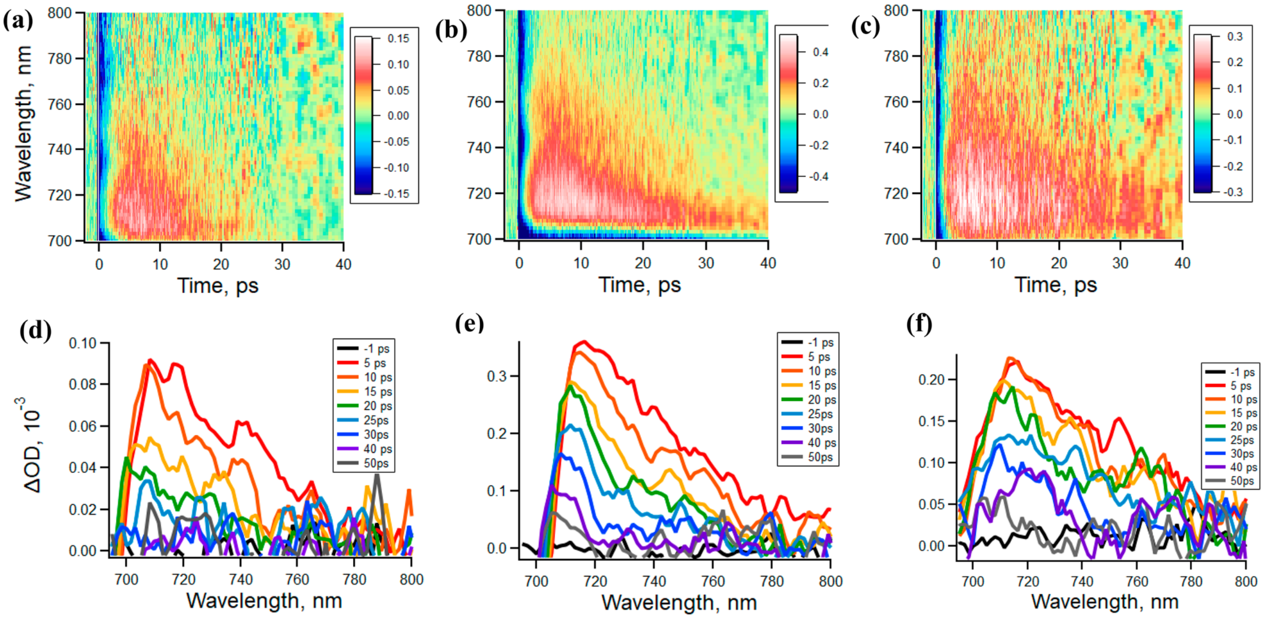

Figure 3. Transient absorption maps in the hot band region for azulene in (a) the hemicarcerand, (b) hexane, and (c) acetonitrile. Transient absorption spectra at different delay times for azulene in (d) hemicarcerand, (e) hexane, and (f) acetonitrile.

From the mechanistic point of view, it is convenient to separate vibrational relaxation into two steps:[2] intramolecular vibrational redistribution (IVR) and VC. As a result of IVR, the energy is redistributed among the vibrational modes within a molecule, creating an equilibrium population, which can be described by the effective intramolecular temperature.[3] The energy subsequently flows from the hot molecule to the cold environment until full thermal equilibrium is achieved. In reality, even though the intra- and intermolecular equilibration processes are distinct, their time scales are not very well separated. Laser spectroscopy experiments on VC were performed as early as the 1970s[21] and 1980s;[22−24] however, the field remains challenging, especially when it comes to electronic excited states. The behavior of vibrationally hot ground states is much more straightforward to monitor and interpret, provided that the selected chromophore is capable of undergoing IC at a faster rate than the subsequent thermal equilibration, $\tau_{IC} < \tau_{VC}$, i.e., within 1 ps or less after photoexcitation. Such ultrafast IC is usually enabled by the presence of a conical intersection between the S_1 and S_0 states, as it is in the classical and spectroscopically accessible case of azulene, which was employed in this study. In contrast, in the aforementioned benzene, the S_1−S_0 IC rate is ∼1000 times slower than the VC, rendering direct spectroscopic detection of the hot ground state impractical. Nevertheless, there is no doubt that the instantaneous molecular temperature of 3000 K

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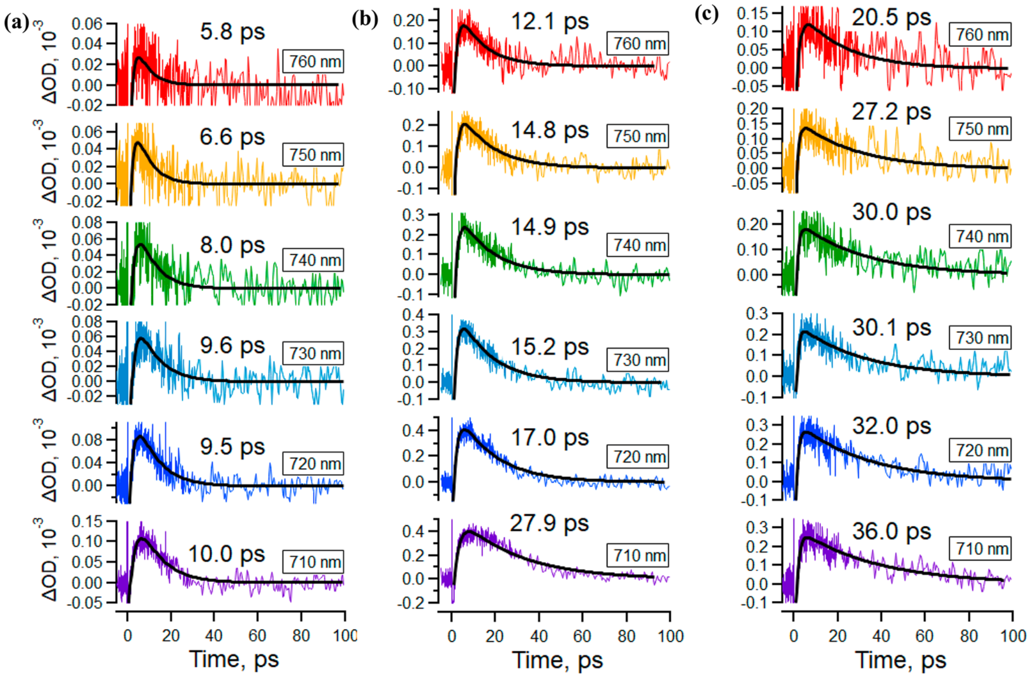

Figure 4. Kinetics of VC of the hot ground state of azulene in (a) the hemicarcerand, (b) hexane, and (c) acetonitrile, at probe wavelengths of 760 (red), 750 (orange), 740 (green), 730 (cyan), 720 (blue), and 760 nm (purple). The biexponential fits are shown in black, with the cooling time constant indicated next to each decay. The complete set of fitting parameters can be found in the Supporting Information.

may exert a major influence on a suitable thermally activated ground-state reaction.

The azulene−hemicarcerand host−guest complex (hemicarceplex) was prepared following the reported procedure.[12] The pump−probe spectroscopy experiments were performed on the host−guest complex as well as free azulene in hexane and acetonitrile. The samples were excited to the S_1 state by ∼55 fs pulses centered at 665 nm and probed with a supercontinuum in the range of 500−900 nm. Detailed descriptions of the experimental setup and conditions are provided in the Supporting Information. The octacarboxy-hemicarcerand molecular cage is soluble in water under mildly basic conditions (pH ≥ 7.5). The hydrophobic and normally not water-soluble azulene spontaneously enters the lipophilic cavity of the hemicarcerand to form the hemicarceplex (Figure 1a). The self-assembly occurs with a time constant of ∼90 min at room temperature,[12] and the resulting hemicarceplex is thermodynamically stable in aqueous solution by up to 10 kcal/mol.[25] The ground-state absorption spectrum of the host−guest complex shown in Figure 1b is similar to that in hexane and exhibits only a slight broadening and a 6 nm red shift, which are attributed to the interactions with the cage.

The transient absorption maps and spectra for azulene in the hemicarcerand, hexane, and acetonitrile are shown in Figure 2. All of the spectra contain similar features. The negative band at 650−700 nm corresponds to the ground-state bleach and resembles the ground-state absorption spectra in Figure 1b. Similarly to the ground-state spectrum, the vibronic structure is less pronounced in acetonitrile. The negative band at 700−800 nm is attributed to stimulated emission from the S_1 state. Its lifetime is approximately 1.5 ps and agrees well with the values reported in the literature.[27,28] Due to the conical intersection,[29] the S_1 state rapidly decays, forming a hot ground state that gives rise to the positive absorption features[24] in the range of 700−780 nm. Lastly, the positive band at 500 nm has been assigned to the S_1−S_2 absorption of azulene.[24] This band is most pronounced for the encapsulated azulene. The decay of the ground-state bleach appears to be significantly slower than the decay of stimulated emission because the hot ground state also contributes to the bleach of the normal S_0−S_1 absorption spectrum.

The transient absorption in the hot ground-state region (700−800 nm) is shown in Figure 3. The initially broad hot band exhibits narrowing and blue shift with time. This is consistent with the diagram of VC shown in Figure 1c. The highest vibrational levels of the hot S_0 state give rise to the red-most part of the spectrum, while the relaxed ones give rise to the blue portion. The decay profiles in the hot band were fitted with a biexponential function (Figure 4). The fast rise of the absorption signal was found to be approximately 1.5 ps, i.e., consistent with the lifetime of the S_1 state. The decaying component is attributed to VC. As seen in Figure 4, all samples exhibited faster decay at longer wavelengths. The difference between the lifetimes at 710 and 760 nm was more pronounced in hexane (27.9 vs 12.1 ps, ratio of 2.3) than that in acetonitrile (36 vs 20.5 ps, ratio of 1.76) or the hemicarceplex (10 vs 5.8 ps, ratio 1.72).

The significant 2−4 fold acceleration of VC in the hemicarceplex assembly is evident in the above data and can be attributed primarily to matching between the densities of the vibrational modes of azulene and its host, which contains 12 phenyl rings with numerous skeletal frequencies similar to those of the guest. The importance of the density of vibrational modes and the frequency matching is corroborated by the large difference between the cooling rates observed in hexane (a large number of mid- and low-frequency modes) and the rigid acetonitrile (a very sparse vibrational spectrum, especially at lower frequencies). Following the approach of Troe et al.[30] and using normal-mode frequencies taken from the literature[16] we calculated the initial vibrational temperature of the hot S_0 state

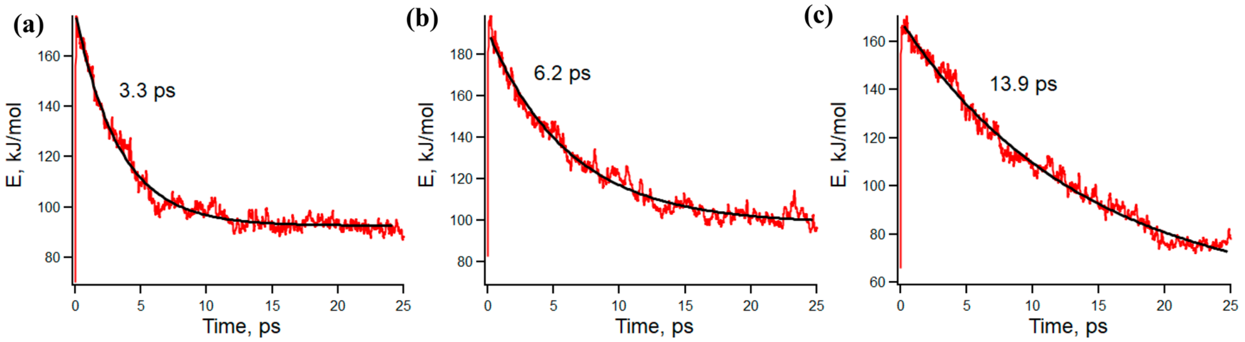

Figure 5. VC trajectories and exponential fits obtained from molecular dynamics simulations (YASARA)[32] of azulene in (a) the hemicarcerand, (b) hexane, and (c) acetonitrile.

azulene to be 1080 K. When the excess energy is redistributed over all available modes of the host−guest assembly, azulene and the hemicarcerand reach thermal equilibrium with one another. At this point, the effective vibrational temperature of the hemicarceplex drops to 378 K. Clearly, the large number of vibrational modes of the hemicarcerand (714 vs 48 for azulene) can very easily accommodate the substantial excess vibrational energy delivered by the hot azulene, resulting in rapid thermal equilibration of the supramolecular complex. The subsequent energy transfer from the cage to the librational and translational degrees of freedom of the solvent has a negligible effect on the overall cooling rate of azulene. The remaining ∼80 K temperature difference between the internally equilibrated hemicarceplex and the solvent is too small to be detected by transient absorption measurements.

In addition to the high density of matching mid- and low-frequency modes, the tight noncovalent binding of azulene in the cage is also likely to contribute to the accelerated VC. The close fit ensures good mechanical coupling between the host and the guest and facilitates the flow of vibrational energy. Indeed, the interior of the hemicarcerand can be thought of as a dense solvent at high pressure. High-pressure experiments in supercritical xenon[24,31] have shown that the rate of VC increases under these conditions.

To support the experimental findings, we performed classical molecular dynamics simulations (for more details, see the Supporting Information). The initial vibrational temperature of azulene was set to 1080 K by rescaling the atom velocities, while the temperature of the environment (either the cage or the solvent) was set to 298 K, and subsequently, the dissipation of the vibrational energy of azulene was tracked. The resulting cooling profiles are well reproduced by a monoexponential function, as shown in Figure 5. The computational cooling time constants of 3.3 ps for the encapsulated azulene, 6.2 ps in hexane, and 13.9 ps in acetonitrile are approximately 2 times faster than the experimental results. Nevertheless, the 1.0:1.9:4.2 ratio of cooling times in the host−guest complex, hexane, and acetonitrile is in remarkably good agreement with the experiment, especially in the long-wavelength part of the spectrum, which reports the hottest states. For example, at 760 nm, the experimental cooling times in the hemicarceplex, hexane, and acetonitrile are 5.8, 12.1, and 20.5 ps, respectively, yielding a ratio of 1.0:2.1:3.5. The MD simulations also reinforce the notion of a close fit of azulene inside of the cavity of the hemicarcerand. Runs as long as 15 ns indicated no large-amplitude reorientation of the guest.

To conclude, pump−probe laser spectroscopy and molecular dynamics simulations show that the VC of the guest molecule can be dramatically accelerated upon encapsulation in a molecular container. The observed cooling rate of the hot S_1 state of azulene trapped within the Cram-type octacarboxyhemicarcerand is by far the fastest of any medium reported in the literature.[24,30,31] The magnitude of the acceleration is likely to depend on specific pairing of the host and guest molecules. Azulene and the octacarboxyhemicarcerand exhibit excellent matching between the frequencies of the skeletal vibrational modes and equally good mechanical coupling resulting from the tight binding. When the dimensions of the host's cavity significantly exceed the size of the guest, the enhanced cooling effect is likely diminished or perhaps even reversed. Indeed, one can envision that in the case of a sufficiently large void the collisions between the hot guest and the walls of the molecular container are so infrequent that the latter may act as an insulator rather than a very effective heat sink, as was seen in this study. This situation may be difficult to achieve experimentally because, in addition to the guest molecule of interest, such large voids would also be able to accommodate solvent molecules.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.9b00406.

> Experimental details, additional time-resolved spectroscopy data, calculations of vibrational temperature of hot ground state, and details of molecular dynamics simulations (PDF)

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Notes

The authors declare no competing financial interest.

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