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Rotational Flexibility in NH_4^+−Encapsulated 18-Crown-6 Studied by Molecular Dynamics and Positron Annihilation: Where Does the Positron Localize?

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Conformational flexibility of the ammonium complex of macrocyclic 18-crown-6 at $100\ \mathrm{K} \leq T \leq 300\ \mathrm{K}$ is studied using a positron microprobe in conjunction with molecular dynamics simulations. The ammonium cation, encapsulated in a three-pointed hydrogen-bonding perching arrangement, undergoes unhindered facile rotation inside the crown cavity, and the ether backbone adopts itself to the dynamic cation conformation. Preferential localization of the positron in the vicinity of the encapsulated cation results in the positron sensing changes in the local electron density distribution arising from the unrestricted rotational motion of the cation as well as from the slow motion of the crown backbone and hence sensing only an average conformation of the complex.

Introduction

Ammonium crown ether complexes are potential candidates for applications in the separation of biologically important protonated amines.[1] The high specificity exhibited by 18-crown-6 in binding ammonium cations is entirely determined by the energetics of the interactions and by the conformations adopted by the crown ether.[2−4] 18-Crown-6 is very flexible and can adopt 675 ideal conformations, of which 190 are potentially favorable ones with only slightly different energies.[5] X-ray crystal structures and spectroscopic evidence show that the crown adopts a C_i symmetric structure in its uncomplexed solid state, whereas a D_{3d} symmetry is observed in solution as well as in its alkali metal (K^+, Rb^+, and Cs^+) complexes.[6] Semiempirical and ab initio calculations have revealed that the C_i structure is the most energetically stable conformation compared to the highly symmetric D_{3d} conformation.[7,8] Despite the extensive literature available on the conformational statistics of 18-crown-6 at ambient temperature in different environments, the conformational flexibility at cryogenic temperatures remains unexplored. A positronium fundamental probe has been used extensively to study the local chain conformations on polymeric backbones[9] and in polymer blends[10] across the glass transition temperatures. Our studies on a polymorphic liquid crystal[11,12] showed that the positron annihilation line shapes provide accurate information on the orientational ordering and configurational changes across the mesophase transitions. This work focuses on the conformational flexibility of NH_4^+−18-crown-6 complex in the temperature range 300−100 K, using positron annihilation line shapes, supported by molecular dynamics calculations.

Materials and Methods

The ammonium complex was prepared by dispersing 0.006 mol of 18-crown-6 in 50 mL of methanol, and to this was added 0.006 mol of ammonium thiocyanate. The solution was stirred for 10 min at 40 °C, left to stir at room temperature until complete dissolution, then filtered, and the solvent was removed on a rotary evaporator to yield purple-colored, needle-shaped crystals. The single-crystal structure of the complex was solved using a Nonius Kappa CAD4 diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) operating in $\omega/2\theta$ scanning mode. Accurate lattice parameters were determined from least-squares refinement of 3418 uniquely measured reflections. The final cycle of full-matrix least-squares refinement was based on 1336 observed reflections ($I > 2\sigma(I)$) and 204 variables of parameters, using *SHELXL-97*.[13] An HPGe detector (EG&G ORTEC, p-type) with an energy resolution of 1.42 keV at the 662 keV γ-line of Cs-137 was used to record the positron annihilation energy spectra. For measurements of the line shape parameter (S), a Gaussian profile analysis around the 511 keV γ-line was employed. Variable temperature measurements utilized a liquid-nitrogen-bath cryostat with a temperature accuracy of 0.1 K.

Molecular dynamics simulations were performed using the simulation package *HyperChem 6.0*. The single-crystal structures were fully optimized using the *Gaussian 98W*[14] program. Molecular mechanics, using the MM2 force field, was used to perform the dynamics simulations in the NVE ensemble at constant temperature and in vacuo. Simulations were carried out over 2 ps with a time step of 0.5 fs.

Results and Discussion

In Figure 1, the ammonium cation is encapsulated in a two-centered, three-pointed hydrogen-bonding perching arrangement and displaced by 1.08 Å from the mean plane of the oxygen atoms. The crown ligand adopts D_{3d} symmetry in complexing the ammonium cation.

Figure 2 shows the variation of the S-parameter in the pristine and the complexed 18-crown-6 with reducing temperature. The S-parameter remains constant below 200 K. The nonuniform change observed for the complex in comparison to the variation

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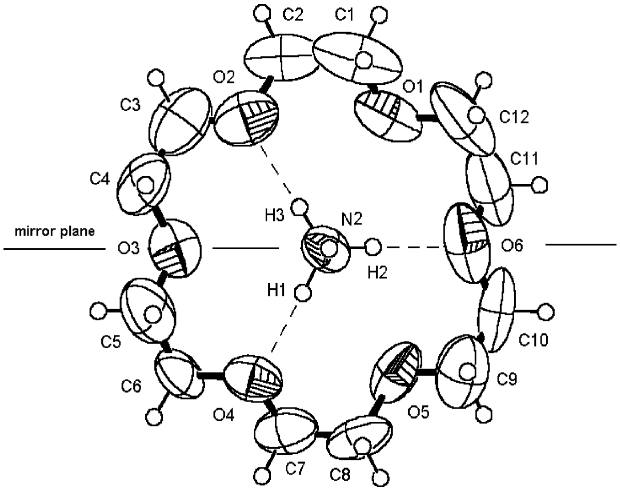

Figure 1. View of the title compound in a direction normal to the mean plane. The displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonding.

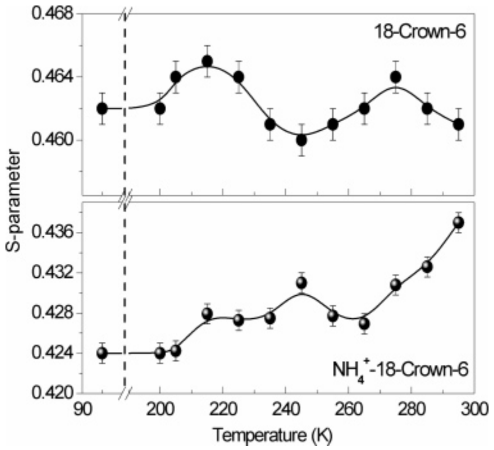

Figure 2. *S*-parameter profile as a function of temperature in pristine and complexed 18-crown-6.

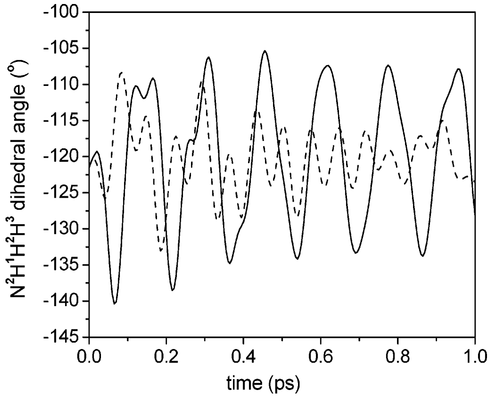

Figure 3. Evolution of the $N^2H^1H^2H^3$ dihedral angle with the simulation times at 300 K (solid line) and 100 K (dashed line).

in the pristine crown indicates that the increase in the symmetry (from C_i to D_{3d}) of the crown backbone in the complex, combined with the cavity occupancy, restricts the rotational flexibility of the oxyethylene linkages.

The flexible nature of the encapsulated ammonium cation studied by molecular dynamics is shown in Figure 3. The variation of the $N^2H^1H^2H^3$ dihedral angle (numbering shown in Figure 1) with simulation times at 300 and 100 K indicates that the cation undergoes facile rotation inside the cavity, even at reduced temperatures. However, no inversion process is observed, proving that the cation remains bonded to the same set of oxygen atoms. This flexibility also remains unhindered in the presence of electrostatic attractions from the thiocyanate anion, but the nonplanar hydrogens of the cation (fourth hydrogen and H1, H2, H3) contribute unequally to the overall rotation.

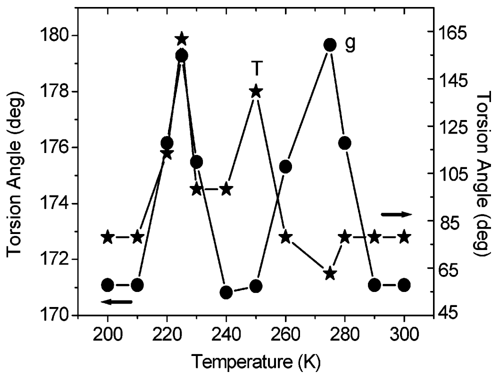

Figure 4. Variation of the trans (T) and the gauche (g) torsion angles of pristine 18-crown-6 with reducing temperature.

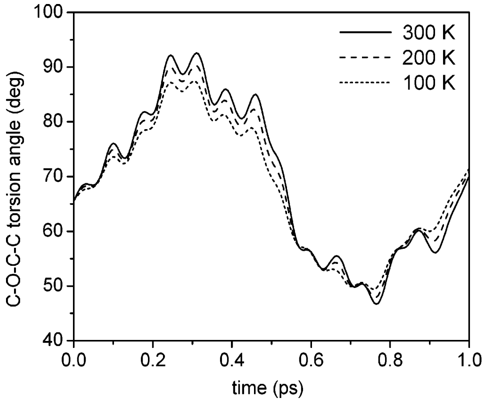

Figure 5. Variation of the C−O−C−C dihedral angle in the ammonium complex with simulation time at different temperatures.

The flexible nature of the crown backbone is classified into contributions from the gauche (g) (around C−O bonds) and trans (T) (around C−C bonds) torsion angles. Temperature-dependent simulations on the C_i structure of the pristine crown, shown in Figure 4, reveal that the gauche torsion angle undergoes large variations with reducing temperature as compared to the trans torsion angle. Thus, the trans torsion was more rigid and did not contribute to the crown conformational flexibility. The excellent agreement between the temperatures corresponding to variations in the gauche torsion angles and those obtained from the *S*-parameter profile indicates that the conformational changes occurring in the pristine crown resulted from a change in the orientation about the C−O bonds only. The variation of this gauche torsional angle in the ammonium complex with simulation time at different temperatures is shown in Figure 5.

The slow and continuous increase and decrease observed at all temperatures, when compared to the rapid rotation of the cation in the same time interval, indicates that the mobility of the crown backbone is as a result of the host adopting itself to a dynamic cation guest. This synchronous motion ensures that the hydrogen bonding between the crown and the cation is maintained, and no inversion process of the cation occurs. Further, a maximum flexibility limit of ±25° from the equilibrium value of 65° can be attributed to the gauche torsion angle. This is in contrast with the higher flexibility limit in the pristine crown and is further evidence of the restriction in the crown flexibility in the complex.

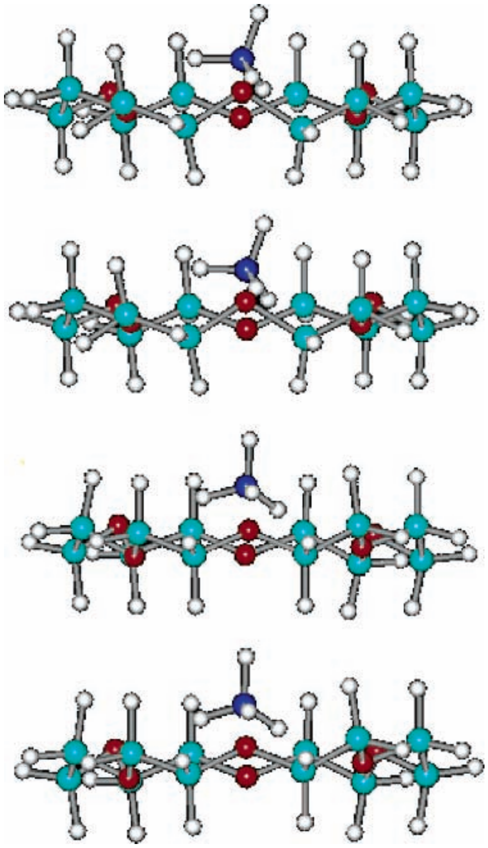

Figure 6. Snapshots of the frozen conformations of the ammonium 18-crown-6 complex (simulation time 0.5 ps) at different temperatures. In descending order: (a) 290, (b) 260, (c) 230, (d) 200 K.

All simulations performed reveal that the overall conformation of the complex is dependent on the conformational mobility of the ammonium cation. Snapshots taken during the simulation runs at different temperatures are shown in Figure 6.

The images reveal that the overall conformation of the complex is identical, except for the orientation of the cation, which changed in the next time frame of the simulation. Thus, the conformation existing at a particular temperature and at a particular time instant does not represent the equilibrium conformation. Nevertheless, the observed variations in the *S*-parameter with temperature are rationalized by considering the annihilation of the positron within the neighborhood of the ammonium ion. A preferential localization of the positron in the vicinity of the cation would result in the positron sensing changes in the local electron density distribution arising from the unrestricted rotational motion of the cation as well as from the slow motion of the oxygen atoms of the crown. This is in contrast to the preferred localization of e^+ around the C−O gauche linkages in the pristine crown. However, the lifetime of the positron (∼nanosecond) is longer as compared to the simulation time (2 ps). Because the rotational flexibility of the cation, and hence that of the complex, occurs on a faster time scale, the positrons encounter only the average molecular configuration before annihilation. The rapidly fluctuating local electron density explains the nonuniform variation of the annihilation line shape.

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