

Photoelectron spectroscopy of hydrated hexafluorobenzene anions

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We present a synergetic experimental/theoretical study of hydrated hexafluorobenzene anions. Experimentally, we measured the anion photoelectron spectra of the anions, $C_6F_6^-(H_2O)_n$ ($n=0-2$). The spectra show broad peaks, which shift to successively higher electron binding energies with the addition of each water molecule to the hexafluorobenzene anion. Complementing these results, we also conducted density functional calculations which link adiabatic electron affinities to the optimized geometric structures of the negatively charged species and their neutral counterparts. Neutral hexafluorobenzene-water complexes are not thought to be hydrogen bonded. In the case of $C_6F_6^-(H_2O)_1$, however, its water molecule was found to lie in the plane of the hexafluorobenzene anion, bound by two $O-H \cdots F$ ionic hydrogen bonds. Whereas in the case of $C_6F_6^-(H_2O)_2$, both water molecules also lie in the plane of and are hydrogen bonded to the hexafluorobenzene anion but on opposite ends. This study and that of Schneider *et al.* [J. Chem. Phys. **127**, 114311 (2007), preceding paper] are in agreement regarding the geometry of $C_6F_6^-(H_2O)_1$. © 2007 American Institute of Physics. [DOI: 10.1063/1.2768349]

INTRODUCTION

The ability of fluorocarbons to form hydrogen bonds has been a subject of debate. For example, based on an analysis of structural databases, several authors concluded that C–F groups are very poor hydrogen bond acceptors.^{1–4} In particular, Dunitz and Taylor noted that out of 5947 C–F bonds reported in the Cambridge Structural Database, only 37 were even possibly involved in C–F \cdots H hydrogen bonding, and of these, only two were definitively found to form hydrogen bonds.¹ On the other hand, it is also known that C–H \cdots F interactions in the crystals of fluorinated organic compounds have structurally directional properties which are analogous to those in other weak hydrogen-bonded systems.^{4–6} Furthermore, gas-phase complexes of water and methanol with *partially* fluorinated benzenes, e.g., monofluorobenzene, 1,4-difluorobenzene, and 1,2,4,5-tetrafluorobenzene, form cyclic hydrogen-bonded complexes with C–H \cdots O–H \cdots F–C structural motifs.^{7–10}

By contrast, a fully fluorinated benzene molecule, i.e., hexafluorobenzene, and a water molecule do not interact to form a hydrogen bond. Calculations by Gallivan and Dougherty¹¹ and by Danten *et al.*¹² on the hexafluorobenzene-water complex both find an initially counterintuitive geometry in which the water molecule sits above the plane of the hexafluorobenzene molecule with its C_{2v} axis perpendicular to the plane of hexafluorobenzene and with the lone pairs of oxygen pointing directly toward the hexafluorobenzene plane. Gallivan and Dougherty characterized their binding as primarily electrostatic with an attractive

interaction between the dipole moment of water and the quadrupole moment of hexafluorobenzene. The same calculations also imply an absence of in-plane C–F \cdots H–O hydrogen bonding interactions, even in face of the availability of hexafluorobenzene's six C–F groups. In addition, circumstantial experimental evidence by Patwari and Lisy (infrared photodissociation in beams) and by Besnard *et al.* (infrared and Raman spectroscopy in solutions) is also consistent with this assessment.^{13,14} Using the atoms in molecules theoretical approach, Singh *et al.*¹⁵ recently showed that C–F groups in fluorinated benzenes lose their abilities to hydrogen bond when benzene is substituted with five or more fluorine atoms. This was attributed to a lowering of peripheral electron densities on the terminal fluorine atoms.¹⁶ In light of the foregoing, an intriguing question arose: Would hexafluorobenzene hydrogen bond to water if the electron density on its fluorine atoms were to be somehow increased? To tackle this question, we added an extra electron to hexafluorobenzene and studied the interaction of the resulting hexafluorobenzene anion with one and with two water molecules. This was accomplished by forming hexafluorobenzene anion-water complexes, $(C_6F_6)^-(H_2O)_{n=1,2}$, and measuring their photoelectron spectra. Complementing these experimental results, we also performed calculations which linked adiabatic electron affinities to the structures of the negatively charged species and their neutral counterparts. Furthermore, as a point of reference, we also conducted photoelectron experiments and calculations on the hexafluorobenzene anion, $C_6F_6^-$ itself, even though its photoelectron spectrum had been reported previously.¹⁷ In a sense, our study of the $(C_6F_6)^-(H_2O)$ system is a mirror image of our earlier studies of the anion-molecule complexes $NO^-(C_6H_6)$ and $O_2^-(C_6H_6)$. In the former case, the molecule from which the anion was

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formed is aromatic and its solvent is a nonaromatic molecule, whereas in the latter cases, the roles are reversed.¹⁸

EXPERIMENTAL AND COMPUTATIONAL METHODS

The experimental portion of this work consisted of generating the solvated cluster anions, $C_6F_6^-(H_2O)_n$ ($n=0-2$), identifying them by mass spectrometry, mass selecting the species of interest, and measuring their anion photoelectron spectra. These cluster anions were produced by the coexpansion of $C_6F_6(g)$, $H_2O(g)$, and argon at a total pressure of 1–4 atm through a 20 μm nozzle into a high vacuum. The resultant jet was intercepted as it left the nozzle by a stream of electrons produced by a biased thoriated iridium filament. This resulted in the formation of a microplasma, which itself was confined by an axial magnetic field. The anionic clusters were then extracted, formed into a beam (focused), and mass analyzed by a 90° sector magnet. The ion of interest was then selected by tuning the magnetic field of the magnet and sent on into a chamber where it was irradiated with photons from an argon ion laser operating intracavity at 488 nm (2.54 eV). The resulting photodetached electrons were next energy analyzed with a hemispherical electron energy analyzer and counted. The photodetachment process is governed by the energy-conserving relationship $h\nu = EBE + EKE$, where $h\nu$ is the photon energy, EBE is the electron binding energy, and EKE is the electron kinetic energy. The experimental apparatus has been described in detail elsewhere.¹⁹ The computational portion of this work focused on calculating the energies of the optimized structures of both the anionic species and their neutral counterparts, thereby providing their corresponding adiabatic electron affinities. These calculations were carried out at the MPW1PW91/6-311++G(*d,p*) level of density functional theory using GAUSSIAN 98.²⁰

EXPERIMENTAL RESULTS

The mass spectrum exhibited strong ion intensities for $C_6F_6^-(H_2O)_n$ at $n=0, 1$, and 2, only weak intensity at $n=3$, and no significant signal for $n>3$. The water cluster anion series $(H_2O)_n^-$ appeared for $n>10$ and was the only series present at higher masses. The photoelectron spectra for $C_6F_6^-(H_2O)_n$, $n=0-2$, are presented in Fig. 1, and all three exhibit broad spectral bands. Information extracted from these spectra is presented in Table I.

Our photoelectron spectrum of $C_6F_6^-$ agrees well with the previously published spectrum recorded by Nakajima *et al.*¹⁷ They reported a peak intensity maximum [vertical detachment energy (VDE)] of 1.56 eV and a threshold energy E_T of 0.80 eV, while we measured a VDE of 1.55 eV and a E_T of 0.7 eV. Our spectrum, however, is considerably better resolved, and the various peaks sticking up out of the otherwise broadband are real and reproducible vibrational features. Nevertheless, our attempts to provide a converged Franck-Condon fit to this spectrum were unsuccessful, probably due to the large number of modes with significant displacements that were encountered. Thus, because of a lack of assignable structure in the spectrum, neither Nakajima *et al.* nor we were willing to report an adiabatic electron affinity

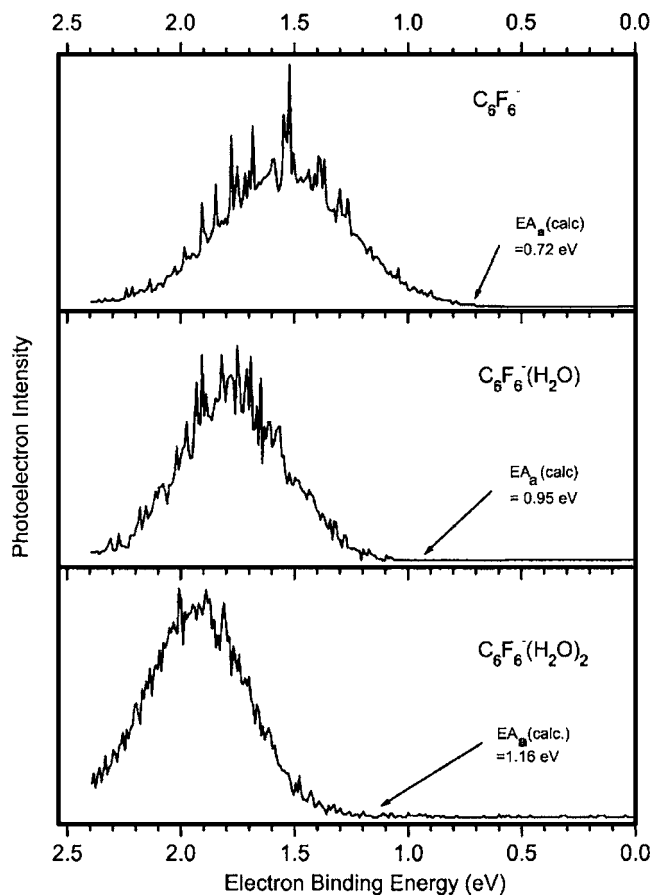


FIG. 1. Photoelectron spectra of the $C_6F_6^-(H_2O)_n$ ($n=0-2$) series.

EA_a value for $C_6F_6^-$, opting instead for giving VDE and E_T values. Three EA_a values for $C_6F_6^-$, however, are reported in the literature. Using a flowing afterglow apparatus, Miller *et al.* determined its EA_a value to be 0.53 eV and also calculated it to be 0.45 eV.²¹ Two purely theoretical studies have also been published. Xie *et al.*²² reported an EA_a for $C_6F_6^-$ of 0.69 eV, while Hou and Huang²³ reported its value to be 0.72–0.76 eV. Still, even without a spectral assignment, if the structural difference between the anion and its corresponding neutral is not too great and if the anions are relatively cold, one would expect the electron binding energy of the EA_a value to be in the neighborhood of the E_T value in an anion photoelectron spectrum, and our E_T value is close to the calculated EA_a values of both Xie *et al.* and Hou and Huang. Nevertheless, because of the expected symmetry difference between neutral C_6F_6 and $C_6F_6^-$ and the lack of reliable information on the temperature of the anions, extracting an EA_a value for $C_6F_6^-$ from the photoelectron spectrum of $C_6F_6^-$ alone remains an uncertain endeavor.

TABLE I. Measured vertical detachment energies, threshold energies, and sequential shifts.

Species	Peak center VDE (eV)	Threshold energy E_T (eV)	Sequential shift ΔVDE (eV)
$C_6F_6^-$	1.55	0.7	
$C_6F_6^-(H_2O)$	1.78	1.1	0.23
$C_6F_6^-(H_2O)_2$	1.93	1.2	0.15

TABLE II. Calculated energies of optimized anionic and neutral structures plus adiabatic electron affinities and vertical detachment energies.

Species	E (a.u.)	ZPE (a.u.)	$E+ZPE$ (eV)	EA_a (eV)	VDE (eV)
C_6F_6	-827.668	0.052	-22520.748	0.724	
$C_6F_6^-$	-827.690	0.047	-22521.472		1.78
$C_6F_6(H_2O)$	-904.107	0.075	-24600.159	0.947	
$C_6F_6^-(H_2O)$	-904.139	0.072	-24601.106		2.23
$C_6F_6(H_2O)_2$ (i)	-980.553	0.100	-26679.697	1.001	
$C_6F_6(H_2O)_2$ (ii)	-980.545	0.097	-26679.544	1.155	
$C_6F_6^-(H_2O)_2$	-980.585	0.095	-26680.699		2.52

While they have slightly narrower widths, the broad photoelectron spectral bands of $C_6F_6^-(H_2O)_1$ and $C_6F_6^-(H_2O)_2$ exhibit the same general shape as the photoelectron spectrum of $C_6F_6^-$, implying that the $C_6F_6^-$ subion is their chromophore for photodetachment and that $C_6F_6^-(H_2O)_1$ and $C_6F_6^-(H_2O)_2$ are both well described as anion-molecule complexes. Moreover, the spectra of $C_6F_6^-(H_2O)_1$ and $C_6F_6^-(H_2O)_2$ shift toward higher EBE values as n increases. This is due to the excess electron of $C_6F_6^-$ being progressively stabilized by solvation (hydration). These sequential shifts carry information about the stepwise solvation energy as one and then another water (solvent) molecules are added to the system. Such shifts are governed by the following relationship:²⁴

$$EA(XY_n) - EA(XY_{n-1}) = D[X^-Y_{n-1} \cdots Y] - D[XY_{n-1} \cdots Y], \quad (1)$$

where $EA(XY_n)$ is the adiabatic electron affinity of XY_n , $EA(XY_{n-1})$ is the adiabatic electron affinity of XY_{n-1} , $D[X^-Y_{n-1} \cdots Y]$ is the dissociation energy for the X^-Y_n cluster anion to lose a single solvent molecule Y (i.e., the negative of the stepwise anion-neutral solvation/interaction energy), and $D[XY_{n-1} \cdots Y]$ is the dissociation energy for the XY_n neutral cluster to lose a single solvent molecule Y (i.e., the negative of the stepwise neutral-neutral solvation/interaction energy).

Next, consider the relationship between VDE and EA_s . The vertical detachment energy is equal to adiabatic electron affinity plus the neutral's reorganization energy λ , i.e., $VDE = EA_a + \lambda$. While we did not measure EA_a per se, we did measure VDE values. The reorganization energies in all three $C_6F_6^-(H_2O)_n$, $n=0-2$, spectra are likely to be similar, both because the chromophore is the same in each case and because the spectral band shapes are empirically similar. Thus, if EA_a values in Eq. (1) are replaced by $VDE - \lambda$, the λ values will roughly cancel, leaving the following sequential shift equation based on differences in VDE values for adjacent size cluster anions:

$$VDE(XY_n) - VDE(XY_{n-1}) = D[X^-Y_{n-1} \cdots Y] - D[XY_{n-1} \cdots Y]. \quad (2)$$

As shown in Table I, we have measured VDE and E_T values for the photoelectron spectra of both $C_6F_6^-(H_2O)_1$ and $C_6F_6^-(H_2O)_2$. The VDE values in Table I lead to the sequential VDE shifts, ΔVDE , from the spectra of $C_6F_6^-$ to $C_6F_6^-(H_2O)_1$ and from the spectra of $C_6F_6^-(H_2O)_1$ to

$C_6F_6^-(H_2O)_2$, and they are 0.23 and 0.15 eV, respectively.

The shift from the spectra of $C_6F_6^-$ to $C_6F_6^-(H_2O)_1$ is $D[C_6F_6^- \cdots H_2O] - D[C_6F_6 \cdots H_2O] = 0.23$ eV. Since Gallivan and Dougherty¹¹ had calculated $D[C_6F_6 \cdots H_2O]$ to be 0.09 eV, $D[C_6F_6^- \cdots H_2O]$ must be 0.32 eV or 7.4 kcal/mole. Thus, our estimate for the solvation (stabilization) energy of $C_6F_6^-$ by a single H_2O molecule is -7.4 kcal/mole. Likewise, the shift from the spectra of $C_6F_6^-(H_2O)_1$ to $C_6F_6^-(H_2O)_2$ is $D[C_6F_6^-(H_2O)_1 \cdots H_2O] - D[C_6F_6^-(H_2O)_1 \cdots H_2O] = 0.15$ eV. Gallivan and Dougherty¹¹ had also calculated $D[C_6F_6^-(H_2O)_1 \cdots H_2O]$ and found it to be 0.07 eV. Thus, $D[C_6F_6^-(H_2O)_1 \cdots H_2O]$ must be 0.22 eV or 5.1 kcal/mole. Thus, our estimate for the stepwise solvation energy of $C_6F_6^-(H_2O)$ by a second H_2O molecule is -5.1 kcal/mole.

COMPUTATIONAL RESULTS

The energies of the optimized structures of both the anionic species and their neutral counterparts are presented in Table II along with their adiabatic electron affinities and vertical detachment energies. Their corresponding geometries are shown in Fig. 2.

Figure 2(a) shows the computed structure of neutral hexafluorobenzene. Addition of an electron to hexafluorobenzene distorts the regular hexagon (D_{6h}) structure of the neutral molecule, resulting in a boatlike structure with C_{2v} symmetry as shown in Fig. 2(b). The most notable structural change upon forming the hexafluorobenzene anion is the bending of the two C-F bonds out of plane by as much as 27° . Furthermore, the carbon skeleton is also slightly distorted, changing the internal dihedral angles of the ring by 2.3° . The structural difference between the neutral and its anion is responsible for the broad Franck-Condon envelope (band) seen in the photoelectron spectrum of $C_6F_6^-$. This same structural difference is also likely to be the primary reason for the width of the bands in the spectra of $C_6F_6^-(H_2O)_1$ and $C_6F_6^-(H_2O)_2$, since $C_6F_6^-$ is the chromophore in both. The adiabatic electron affinity that we calculated for C_6F_6 is 0.72 eV, in good agreement with the calculated values of Xie *et al.*²² and Hou and Huang.²³ The vertical detachment energy that we calculated for $C_6F_6^-$ is 1.78 eV, in reasonable accord with our experimental value of 1.55 eV.

The computed structure of neutral hexafluorobenzene-water complex is presented in Fig. 2(c). It shows the water molecule binding above the plane of C_6F_6 with the oxygen atom of the water molecule pointing directly toward the π

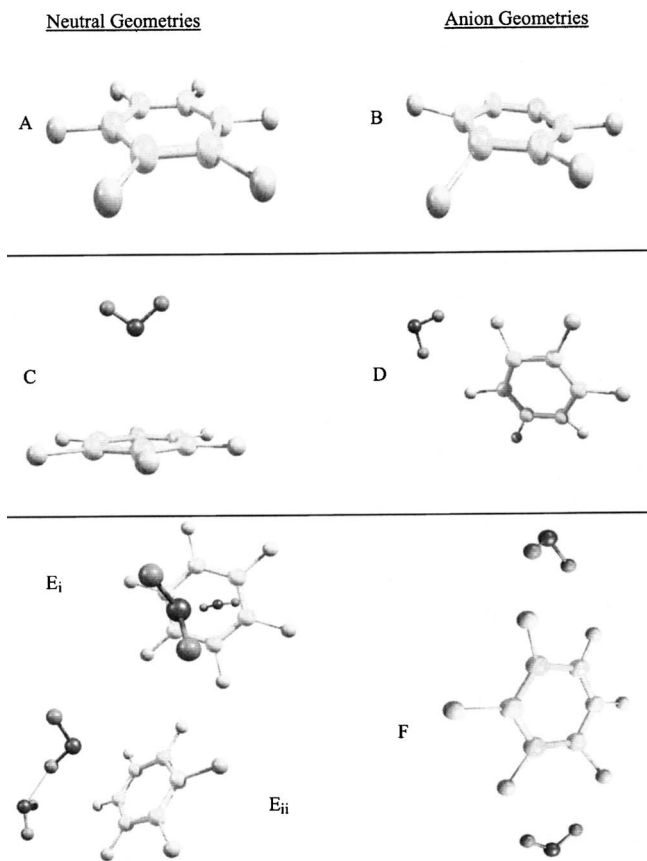


FIG. 2. Optimized anionic and neutral structures: (A) C_6F_6 , (B) $C_6F_6^-$, (C) $C_6F_6(H_2O)_1$, (D) $C_6F_6^-(H_2O)_1$, [(E_i) and (E_{ii})] $C_6F_6(H_2O)_2$, and (F) $C_6F_6^-(H_2O)_2$.

system of the hexafluorobenzene, in agreement with the structure reported in the literature.^{11,12} Starting from the neutral complex, the structural optimization of the hexafluorobenzene-water anionic complex leads to the migration of the water molecule into the plane of hexafluorobenzene and the formation of two O–H···F hydrogen bonds. The adiabatic electron affinity that we calculated for $C_6F_6(H_2O)_1$ is 0.95 eV. The vertical detachment energy that we calculated for $C_6F_6^-(H_2O)_1$ is 2.23 eV, in acceptable agreement with our experimental value of 1.78 eV.

The computed structure of neutral $C_6F_6(H_2O)_2$ minimizes into two structures. In the first one, the two water molecules are bound one above and one below the ring [see Fig. 2(E_i)]. In the other structure, one water molecule is bound to the π system of the hexafluorobenzene, and the other water molecule is hydrogen bonded to it [see Fig. 2(E_{ii})]. This structure can also be viewed as a water dimer bound to hexafluorobenzene, and in any case, it is the most stable structure. Starting from either neutral geometry, however, the structural optimization of $C_6F_6(H_2O)_2$ converges to that shown in Fig. 2(f). There, both water molecules are hydrogen bonded to the hexafluorobenzene anion but on opposite ends. The adiabatic electron affinity that we calculated for $C_6F_6(H_2O)_2$ is 1.16 eV. The vertical detachment energy that we calculated for $C_6F_6^-(H_2O)_2$ is 2.52 eV, in rough accord with our experimental value of 1.93 eV. Furthermore,

in the cases of both $C_6F_6^-(H_2O)_1$ and $C_6F_6^-(H_2O)_2$, our calculations show their hexafluorobenzene anion moieties retaining their nonplanar structures.

DISCUSSION

Our calculations link adiabatic electron affinities and vertical detachment energies to the optimized geometries of the three anionic species we studied and their neutral counterparts. The locations of these calculated EA_a values are marked on each of our photoelectron spectra in Fig. 1. In all three cases, they are seen to lie quite close to the spectral threshold energies E_T (see Table I). Especially in light of the fact that our measured E_T value from the photoelectron spectrum of $C_6F_6^-$ is close to all three calculated values for the EA_a of C_6F_6 (Xie *et al.*,²² Hou and Huang,²³ and this work), we see our calculated EA_a values for the three systems we studied as being consistent with their measured anion photoelectron spectra. Likewise, our measured and calculated vertical detachment energies are consistent with one another. Thus, the experimental results authenticate the computed geometries and thereby support our structural assignments.

In the case of the hexafluorobenzene-water anionic complex, $C_6F_6^-(H_2O)_1$, the water molecule is seen to lie in the plane of hexafluorobenzene anion, bound by two O–H···F ionic hydrogen bonds, whereas in the case of the dihydrated hexafluorobenzene anion case, $C_6F_6^-(H_2O)_2$, both water molecules are also hydrogen bonded to the hexafluorobenzene anion but on opposite sides. Thus, even though neutral hexafluorobenzene-water complexes are not bound by hydrogen bonding, their anionic hexafluorobenzene-water complexes are, i.e., a hexafluorobenzene molecule hydrogen bonds with water in the presence of an excess electron.

One can describe the role of the excess electron in two ways: (1) As causing an enhancement of electron density on the fluorine atoms of hexafluorobenzene or (2) as a monopole-dipole interaction due to electron attachment to hexafluorobenzene and the formation of the $C_6F_6^-$ anion. While these two pictures are not incompatible, the simple monopole-dipole model no doubt misses much of the structural detail of the interaction. Also, the fact that an anion interacts with a hydrogen atom (or atoms) at the positive end of a molecular dipole does not negate it having hydrogen bonding character. An example is the case of $H^-(NH_3)$, where the hydride anion interacts with one (according to theory) of the ammonia molecule's hydrogen atoms, largely through ionic hydrogen bonding.²⁵ There, the interaction energy was measured to be 0.36 eV, where in the case of $C_6F_6^-(H_2O)_1$, the interaction energy between $C_6F_6^-$ and H_2O is 0.32 eV, and in the case of $C_6F_6^-(H_2O)_2$, the interaction energy between $C_6F_6^-(H_2O)_1$ and H_2O is 0.22 eV.

Qualitatively, the present study reaches the conclusion that hexafluorobenzene does indeed hydrogen bond with water in the presence of an excess electron, while quantitatively, it provides values for interaction energies. In the companion paper by Schneider *et al.*²⁶ on the infrared spectroscopy of anionic hydrated fluorobenzenes, they and we reach the same conclusion as to the geometric structure of the hexafluorobenzene-monohydrate anion, $C_6F_6^-(H_2O)_1$. Lastly,

it is interesting to imagine how additional water molecules will add to $C_6F_6^-$, especially once the in-plane sites are filled. Will the first solvent shell exhibit both in-plane, hydrogen bonded and out-of-plane, non-hydrogen-bonded (dipole-quadrupole/lone pair π cloud) interactions?

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