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One-Photon Mass-Analyzed Threshold Ionization Spectroscopy of Bis(η^6-benzene)chromium and Its Benzene and Ar Clusters

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The one-photon mass-analyzed threshold ionization (MATI) spectroscopy of bis(η^6-benzene)chromium is reported. The adiabatic ionization energy is accurately measured to be 44 087 ± 5 cm^{-1} (5.4661 ± 0.0006 eV). The Cr−benzene stretching vibrational mode in the ion with a fundamental frequency of 264 cm^{-1} is found to be optically active. The MATI spectra of bis(η^6-benzene)chromium·Ar and bis(η^6-benzene)chromium·benzene clusters are also reported to give ionization potentials of 43 941 ± 5 cm^{-1} (5.4480 ± 0.0006 eV) and 42 576 ± 5 cm^{-1} (5.2788 ± 0.0006 eV), respectively. A van der Waals mode with the fundamental frequency of 65 cm^{-1} is optically active in the MATI spectrum of the bis(η^6-benzene)chromium·benzene cluster, suggesting an intermolecular structural change upon ionization. The larger bis(η^6-benzene)chromium·(benzene)$_n$ ($n = 2-9$) clusters are found to be generated in the molecular beam. Their ionization potentials, from photoionization efficiency spectra, show the gradual decrease as the cluster size gets larger, down to the value of 5.02 eV for $n = 9$.

I. Introduction

Gas-phase studies of transition metal−molecule complexes have provided the unique opportunity to give insights into the molecular structure and bonding characteristics of those important compounds without complexity due to surrounding solvents.[1] Metal−benzene complexes have been spotlighted especially because their intriguing sandwich-like structures are closely related to catalytic and biological activities.[2−4]

Bis(η^6-benzene)chromium, $Cr(C_6H_6)_2$, is an 18-electron closed-shell compound having two benzene rings with Cr in the center, which is one of the most prototypical examples of organometallic sandwich complexes. Since its discovery in 1955,[5] $Cr(C_6H_6)_2$ has been the subject of extensive studies in terms of its catalytic chemistry and structural properties. And also, its high symmetry of D_{6h} makes this relatively large molecule a good model for many kinds of quantum mechanical calculations.[6−8] Laser spectroscopy and dynamics of bis(η^6-benzene)chromium in the molecular beam have also been extensively investigated because of its intriguing dynamic simplicity despite of its intrinsic complexity as a large chemical system.[9−13]

Ionization dynamics of $Cr(C_6H_6)_2$ has got special attention because many high n-Rydberg states are readily accessible by the UV laser source.[10,12,13] A number of Rydberg bands just below the ionization threshold have been identified by Even et al.[10] Quite recently, Ketkov et al.[12,13] reported an extensive study on vibrational bands associated with the lowest Rydberg p state of $Cr(C_6H_6)_2$ and its deuterated isotopic compounds. Though the ionization dynamics seem to be well-understood from these previous other studies, the ion spectroscopy of $Cr(C_6H_6)_2$ still lacks in terms of its vibrational frequency and the structural change upon ionization. Here, we present one-photon mass-analyzed threshold ionization (MATI) spectrum of $Cr(C_6H_6)_2$ for the first time. Since the ionization level is reached by the one photon process, any complexity associated with intermediate levels could be avoided to provide a nice and simple ionic vibrational spectrum. Additionally, we report here MATI spectra of $Cr(C_6H_6)_2\cdot Ar$ and $Cr(C_6H_6)_2\cdot(C_6H_6)$ clusters. Especially, for the latter, many van der Waals modes are found to be optically active, meaning that the removal of an electron induces the intermolecular structural change of the cluster. The larger $Cr(C_6H_6)_2\cdot$(benzene)$_n$ ($n = 2-9$) clusters are also found to be generated in the molecular beam. These clusters may provide nice model systems for the study of π-stacking property of aromatic systems.

II. Experimental Section

The detailed experimental setup has been previously described.[14,15] Briefly, bis(η^6-benzene)chromium (Aldrich) was heated to 100 °C, mixed with the Ar or Ne carrier gas, and expanded into vacuum through a 0.8 mm diameter nozzle orifice. A tunable laser pulse in the 220−227 nm range was generated by the frequency doubling of the dye laser output (Lambda Physik, Scanmate 2) induced by the 355 nm pumping of a Nd:YAG laser (Spectra-Physics, GCR-150). Molecules excited to MATI states via the one-photon absorption process were allowed to stay for ~10 μs in the presence of a spoil field of 0.5−1 V/cm and ionized by applying a pulsed electric field of 20−80 V/cm. MATI ions were then accelerated, drifted along the field-free region, detected by dual microchannel plates (MCP, Jordan),

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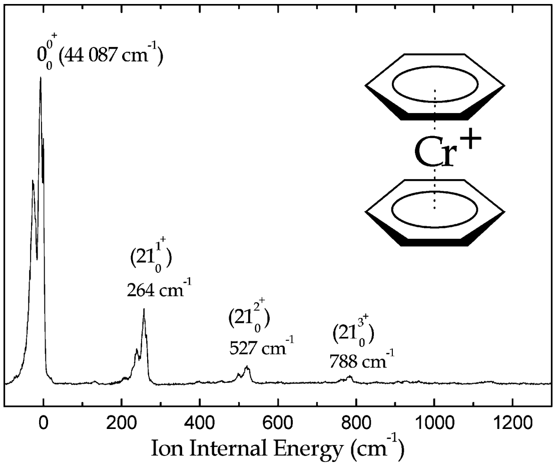

Figure 1. The MATI spectrum of bis(η^6-benzene)chromium. A series of the benzene−Cr stretching modes (ν_{21}) is clearly observed. Shoulder peaks are ascribed to autoionizing rotational levels (see the text).

and A/D converted by an oscilloscope (LeCroy 9361), and the data were stored in a personal computer, which also controlled the dye laser and home-built autotracker in which the second harmonic generation via a KD*P crystal is made.

III. Results and Discussion

The MATI spectrum of $Cr(C_6H_6)_2$ gives an accurate adiabatic ionization potential (IP) of 44 087 ± 5 cm^{-1} (5.4661 ± 0.0006 eV) (Figure 1). The spectral position of the origin band has been measured at several different ionization electric fields (F) to determine the true ionization threshold by extrapolating the measured IP to the value at the zero electric field ($\Delta E \sim 0.5$ cm^{-1} $F^{1/2}$). The intrinsic broad MATI bandwidth (fwhm ~ 2 cm^{-1}) and laser calibration accuracy (±1 cm^{-1}) are mainly responsible for the uncertainty of the reported IP. Shoulder peaks at energies lower than IP are ascribed to autoionizing rotational levels.[9,10] Here, in this case, internal energy associated with the nuclear motion of $Cr(C_6H_6)_2$ in the ground state is transferred to the electronic energy used for the molecular ionization. The IP in this work is quite close to the value of 44 090 cm^{-1} determined earlier from high-n Rydberg series.[10] A series of the totally symmetric Cr−benzene stretching band (ν_{21})[12,13] is clearly observed with the fundamental frequency of 264 cm^{-1} for $Cr(C_6H_6)_2{}^+$. Vibrational energies of the first and second overtone bands, 527 and 788 cm^{-1}, respectively, indicate that the potential along the Cr−benzene stretching mode is quite harmonic. No other vibrational mode is found to be optically active in this one-photon MATI spectrum, indicating that the geometrical change upon ionization of $Cr(C_6H_6)_2$ is little, especially for benzene moieties. The strong MATI origin band in Figure 1 suggests that the difference in the Cr−benzene distance is rather small between the neutral and ionized forms. These experimental observations are consistent with the electronic nature of the ionization of $Cr(C_6H_6)_2$, the removal of an electron in the nonbonding d-orbital of Cr.[9−11] And also, the experiment is consistent with the theoretical prediction that the Cr−ring distance remains constant in the ionization of $Cr(C_6H_6)_2$.[6,8] It is interesting to note that the ν_{21} vibrational frequency (263 cm^{-1}) in the $3d_{z^2}$−$R4p_{x,y}$ Rydberg transition[12,13] is almost identical to that in the cationic ground state.

In Figure 2a, the MATI spectrum of the $Cr(C_6H_6)_2$·Ar cluster is shown to give the ionization energy of 43 941 ± 5 cm^{-1} (5.4480 ± 0.0006 eV). The red shift of IP from the bare $Cr(C_6H_6)_2$ indicates that $Cr(C_6H_6)_2{}^+$ is ~146 cm^{-1} more stabilized by clustering with Ar compared to the neutral ground $Cr(C_6H_6)_2$·Ar cluster. This is quite similar to the IP shift of ~173 cm^{-1} reported for the benzene·Ar cluster with respect to that of benzene,[16] suggesting that Ar may be attached on the plane of the benzene moiety of $Cr(C_6H_6)_2$. No discernible van der Waals band is observed in the MATI spectrum, indicating that there is little structural change upon ionization of the $Cr(C_6H_6)_2$·Ar cluster.

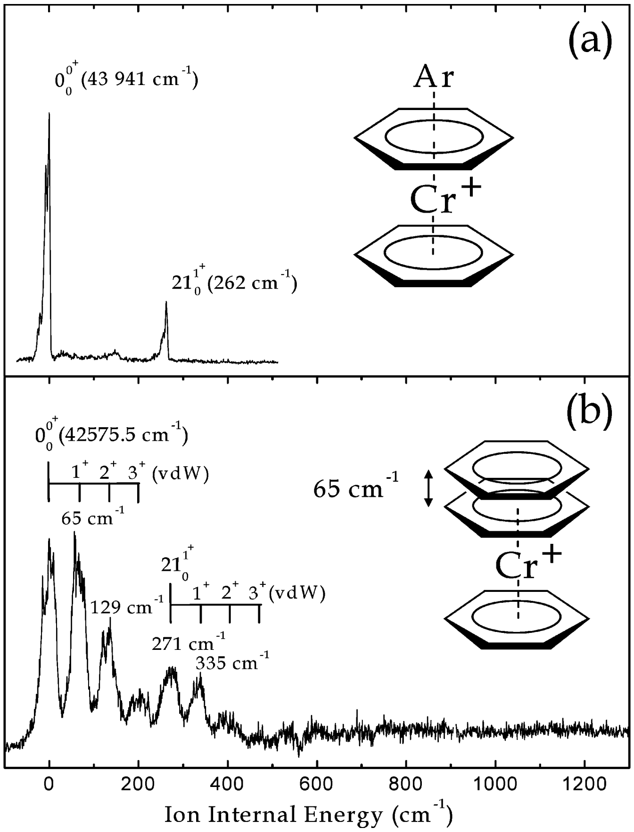

Figure 2. The MATI spectrum of (a) bis(η^6-benzene)chromium·Ar and (b) bis(η^6-benzene)chromium·(benzene). A series of van der Waals modes with a fundamental frequency of 65 cm^{-1} is strongly observed in part b. The shaper band shapes in part a compared to those in Figure 1 are due to the colder beam condition in the former case, where the higher backing pressure is used to produce the clusters in the beam.

Benzene molecules freed from $Cr(C_6H_6)_2$ in the partly occurring decomposition process in the sample chamber are found to undergo the cluster formation with $Cr(C_6H_6)_2$ in the supersonic jet. As a prototypical case for the aromatic π−π interaction, the benzene dimer has long been investigated both extensively and intensively.[17] In the $Cr(C_6H_6)_2$·(benzene)$_n$ cluster, the intermolecular interaction is also the π−π type but somewhat unique in the sense that it is through a neighboring metal atom that should affect the charge density of the benzene moiety of $Cr(C_6H_6)_2$ clustering with solvent benzene molecules. The MATI spectrum of the $Cr(C_6H_6)_2$·(benzene) cluster (Figure 2b) gives an ionization potential of 42 576 ± 5 cm^{-1} (5.2788 ± 0.0006 eV). On the contrary, in the case of the $Cr(C_6H_6)_2$·Ar cluster, a series of van der Waals bands with the fundamental frequency of 65 cm^{-1} is strongly observed. The Cr−benzene stretching frequency of $Cr(C_6H_6)_2$·(benzene)$^+$ is identical to that of $Cr(C_6H_6)_2{}^+$ within experimental uncertainties, and thus, the Cr−benzene ring distance seems not to be modified by the addition of a benzene molecule. Considering the fact that $Cr(C_6H_6)_2$ itself is the stable 18-electron molecule, Cr is less likely to form a metal−ligand bond with additional benzene molecule in the $Cr(C_6H_6)_2$·(benzene) cluster. The solvent benzene molecule is thus likely to be placed on the benzene ring of $Cr(C_6H_6)_2$ in the cluster.

It is well-known that there is a strong charge-transfer from Cr to benzene in neutral $Cr(C_6H_6)_2$, for instance, giving a Mulliken charge of $+0.80$ for Cr, according to the work by Sahnoun and Mijoule.[6] Therefore, even in the neutral $Cr(C_6H_6)_2$·(benzene) cluster, the interaction between benzene and the benzene moiety of $Cr(C_6H_6)_2$ cannot be ascribed to dispersive forces. For instance, the Mulliken charge of -0.121 and $+0.05$ is found for the individual C and H atoms of $Cr(C_6H_6)_2$,[6] respectively, meaning that the benzene ring of $Cr(C_6H_6)_2$ is negatively charged due to the strong metal−ligand charge transfer.[6] Therefore, as found for the benzene dimer ion,[17] the electrostatic charge resonance interaction should be more responsible for the formation of the $Cr(C_6H_6)_2$·(benzene) cluster. Naturally, it is most plausible then that the structure of the $Cr(C_6H_6)_2$·(benzene) cluster adopts the parallel sandwich geometry, as depicted in Figure 2b, similarly to the case of $(C_6H_6)_2{}^+$.[17] When $Cr(C_6H_6)_2$ is ionized, the Mulliken charge of Cr is decreased to $+0.68$, while those of individual C and H atoms become -0.08 and $+0.107$, respectively, implying that the effective charge depletion mainly occurs from the benzene moiety.[6] This somewhat large change in the charge delocalization in $Cr(C_6H_6)_2{}^+$ may lead to the geometrical change of the $Cr(C_6H_6)_2$·(benzene) cluster upon its ionization. However, the simple Mulliken charge analysis does not give enough information for the geometrical change of the cluster upon ionization. For instance, the AIM atomic charges calculated from density-functional theory give corresponding values [for $Cr(C_6H_6)_2$, Cr, $+0.993$; C, -0.167; H, $+0.092$; and for $Cr(C_6H_6)_2{}^+$, Cr, $+1.121$; C, -0.163; H, $+0.156$][8] quite different from those obtained from the Mulliken analysis. Our experimental findings indicate that the intermolecular interaction of benzene and $Cr(C_6H_6)_2$ is stronger in the ion than that in the neutral (vide infra) and the ionization of the $Cr(C_6H_6)_2$·(benzene) cluster is accompanied by a certain geometrical change in terms of the intermolecular displacement. In the present work, we suggest that the 65 cm^{-1} band observed in Figure 2b is ascribed to the $Cr(C_6H_6)_2{}^+$−benzene intermolecular stretching mode. That is, as $Cr(C_6H_6)_2$·(benzene) is ionized, the intermolecular distance between $Cr(C_6H_6)_2$ and benzene becomes shorter to give the MATI spectrum with many overtones of the benzene−$Cr(C_6H_6)_2{}^+$ stretching mode.

It is interesting to compare our results with the case of benzene dimer, though the direct comparison would not be appropriate because of the intramolecular charge transfer occurring in $Cr(C_6H_6)_2$. The MATI or ZEKE (zero-electron kinetic energy) spectrum of the benzene dimer has never been successfully obtained, possibly because of its large structural change[17−19] from a T-shaped or parallel-displaced geometry of the neutral benzene dimer to a parallel-sandwich geometry in the benzene dimer ion.[17−19] Therefore, the fact that we could successfully obtain the MATI spectrum of the $Cr(C_6H_6)_2$·(benzene) cluster itself may indicate that the geometrical change of $Cr(C_6H_6)_2$·(benzene) in the ionization process is not so dramatic, and this may support the parallel-sandwich geometry for both neutral and cationic forms of $Cr(C_6H_6)_2$·(benzene). The IP of $Cr(C_6H_6)_2$·(benzene) is ~1511 cm^{-1} red-shifted from that of $Cr(C_6H_6)_2$ (Figures 1 and 2b). This shift is less than that of $(benzene)_2$ (~4920 cm^{-1}), while much larger than the further shift of ~558 cm^{-1} of $(benzene)_3$.[20] The red-shift of IP represents how much more the cluster is stabilized in the ionic state compared to the cluster stabilization in the neutral state. Therefore, qualitatively speaking, the above experimental fact suggests that the extent of stabilization of $Cr(C_6H_6)_2$·(benzene) by ionization is less than that of the benzene dimer, while it is more than that induced by the addition of one more benzene to the benzene dimer. In $(benzene)_2{}^+$, the charge−resonance interaction is largely responsible for the cluster ion stabilization, while the stabilization by the additional benzene molecule in $(benzene)_3{}^+$ is ascribed to the polarization effect.[17,21] This more evidence that the stabilization in $Cr(C_6H_6)_2$·(benzene)$^+$ is not merely due to the "solvent" polarization effect. The close interaction of the benzene molecule with the charge-transferred ring moiety of $Cr(C_6H_6)_2$ should be responsible for the cluster formation, as proposed above. For the minimum energy structure, however, theoretical calculation is definitely needed, since there could be many other local minimum structures and these should be investigated further.

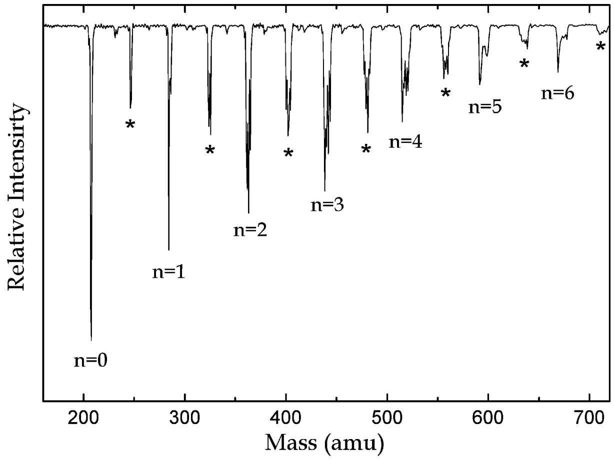

Figure 3. TOF mass spectrum of bis(η^6-benzene)chromium·$(benzene)_n$ clusters taken at $\lambda_{ex} = 223.7$ nm. Peaks denoted with asterisks are due to $Cr(C_6H_6)_2$·$(benzene)_n$·Ar clusters. It is interesting to note that clusters with only a single Ar atom are populated. Broadening of mass peaks as n increases is due to widening of the isotope distribution.

Lowering the excitation energy makes possible the observation of a new type of organometallic cluster, $Cr(C_6H_6)_2$·$(benzene)_n$ ($n = 2-9$) (Figure 3). For these larger clusters, MATI spectra could not be obtained as for the present work. The difficulty comes from the fact that the stronger spoil field is needed to separate out the MATI signal of these larger clusters and the strong spoil field destroys lots of ZEKE states.[18,19] Furthermore, photoionization efficiency (PIE) spectra of these clusters show smoothly rising behaviors in the ionization threshold region, implying that a large structural change may take place upon ionization (Figure 4). It should be noted that the PIE spectrum of a particular $Cr(C_6H_6)_2$·$(benzene)_n$ cluster can be easily contaminated by the dissociative ionization of $Cr(C_6H_6)_2$·$(benzene)_{n+1}$, especially when $n > 4$. Therefore, we adjusted the molecular beam condition to minimize the population of the larger ($>n$) clusters when the PIE spectrum of $Cr(C_6H_6)_2$·$(benzene)_n$ is recorded. This experimental effort provides the graph in Figure 5, showing a gradual decrease of $\Delta IP = IP_n - IP_{n-1}$ as the number of benzene solvent molecules increases. The decrease of IP and the convergence to a certain value upon increasing the cluster size is frequently observed in many different types of clusters such as metal clusters[22] and hydrogen-bonded organic clusters.[23] That is, as the number of solvent molecules increases, the role of benzene molecules as the solvent seems to be apparent. The interesting experimental finding is that no clusters with more than one Ar atom are populated in the jet (Figure 3). The $Cr(C_6H_6)_2$·$(benzene)_n$·Ar clusters show a similar small red-shift in their IP's compared to those of their corresponding $Cr(C_6H_6)_2$·$(benzene)_n$ clusters

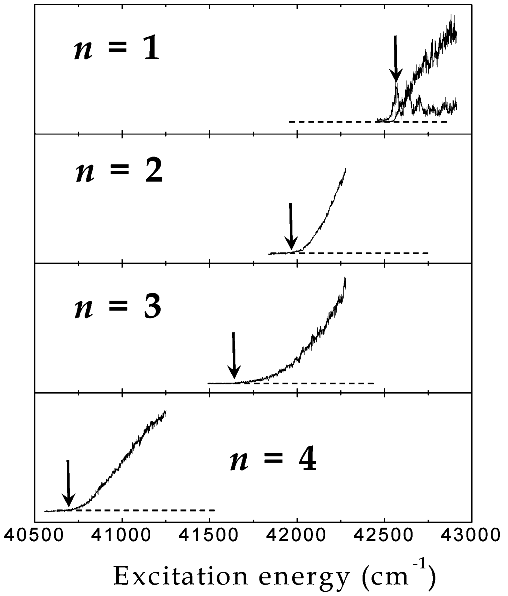

Figure 4. Photoionization efficiency (PIE) spectra of $Cr(C_6H_6)_2 \cdot (benzene)_n$ for $n = 1, 2, 3$, and 4. For $n = 1$, The MATI spectrum of $Cr(C_6H_6)_2 \cdot (benzene)$ is shown on the same energy scale for the comparison. The onset energy of the PIE spectrum corresponds to the MATI origin peak position within ±25 cm^{-1}.

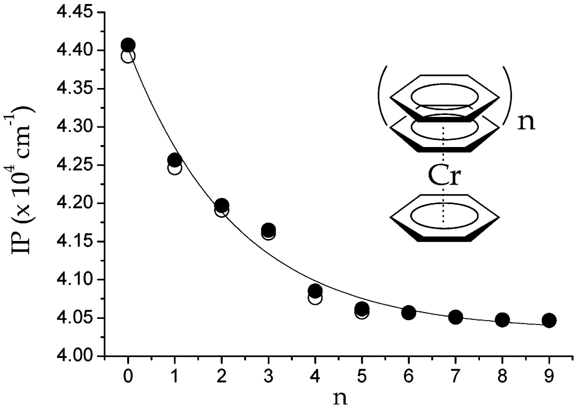

Figure 5. Ionization potentials as a function of the size of $Cr(C_6H_6)_2 \cdot (benzene)_n$ clusters (close circles) and $Cr(C_6H_6)_2 \cdot (benzene)_n \cdot Ar$ clusters (open circles). The exponential decaying solid curve is drawn just to show the trend of IP versus *n*. Uncertainties are within the areas of the circles.

(Figure 4), suggesting that the Ar may be attached to one of two benzene rings of $Cr(C_6H_6)_2$ while the benzene solvent molecules gather around the other ring of $Cr(C_6H_6)_2$. This observation might be closely related to the cluster formation mechanism such as $(C_6H_6)_n + Cr(C_6H_6)_2 \rightarrow Cr(C_6H_6)_2 \cdot (C_6H_6)_n + Ar \rightarrow Cr(C_6H_6)_2 \cdot (C_6H_6)_n \cdot Ar$. And yet, this conjecture is subject to further detailed investigation. Present work does not provide direct information about microscopic structures of clusters. However, if reasonable calculation can be carried out for this system, it will quite helpful to compare the experimental result of this work with the theory.

IV. Summary and Conclusion

MATI spectroscopy of bis(η^6-benzene)chromium and its Ar and benzene clusters are reported to give precise ionization potentials of 5.4661, 5.4480, and 5.2788 eV, respectively. The structure of the bis(η^6-benzene)chromium·benzene cluster may adopt the parallel-sandwich geometry in both neutral and cationic forms, due to the strong charge-transfer characteristics of the organometallic compound. The large bis(η^6-benzene)-chromium·(benzene)$_n$ ($n = 2-9$) clusters show the gradual decrease of the ionization potential as the cluster size gets larger. The present sandwich complex and associated clusters provide a unique opportunity for the study of aromatic $\pi-\pi$ interaction and also the metal−ligand charge-transfer process. Theoretical calculation would be desirable to stimulate the further experimental investigation of these interesting systems.

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