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# Theoretical study of femtosecond pump–probe signals of nonstoichiometric alkali halide clusters

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**Abstract.** We present the outline of the *ab–initio* molecular dynamics method for adiabatic excited states which is suitable to treat the involved excited electronic states simultaneously with the motion of the nuclei. The method allows the simulation of time–resolved pump–probe signals and the analysis of the signals in terms of the underlying nuclear dynamics. Moreover, the timescales of the structural relaxation in excited electronic states vs. intramolecular vibrational relaxation processes can be estimated and the influence of the initial temperature of the cluster can be determined.
The method is applied to the analysis of the timescales as well as of the dynamics of localized/delocalized electronic excitations in the $Na_2F$ molecule which represents a test example for nonstoichiometric alkali–halides with one excess electron. The aim is to develop a method for the investigation of time–dependent laser induced processes in clusters which is capable to extract the leading physical effects responsible for the controlled excitation dynamics and for the evolution of the non–equilibrium states.

**PACS.** 31.15.Ar Ab initio calculations – 31.15.Qg Molecular dynamics and other numerical methods – 31.50.+w Excited states – 31.70.Hq Time-dependent phenomena: excitation and relaxation processes and reaction rates

## 1 Introduction

Clusters are of considerable interest in the context of ultrafast spectroscopy since they constitute finite systems where the number of degrees of freedom can be continuously varied by changing the cluster size. In this way, the "transition" from resonant dynamics to dissipative dynamics can be investigated by increasing the cluster size. Moreover, the nuclear dynamics allows for a separation of the timescales between high–frequency, such as intramolecular, and/or low–frequency, such as intermolecular motions in clusters.

In the previous work we developed a multi state femtosecond dynamics involving the ground states of the negative ion, the neutral and the positive ion of $Ag_3$ [1]. It was prooved to be very promising for the extension involving excited electronic states since our results were able to interpret the experimental NENEPO (negative ion-to neutral to-positive ion) femtosecond spectra of $Ag_3$ [2]. Moreover, our approach gave more information which were not accessible in experimental work until now and therefore, they present a stimulation for new experiments. In this paper we extend the method and present its first application to multi state femtosecond dynamics of small clusters involving the *adiabatic excited electronic states.* We address the following time–resolved pump–probe experimental situation: Initially, a thermal ensemble of molecules in the electronic ground state is assumed. Optical excitation by the pump pulse is considered in order to prepare a transition state on a particular *excited electronic state* of the molecule. The subsequent dynamics of the molecule in this state is monitored by ionizing the molecule via a second time delayed probe pulse. This approach is promising for the investigation of the structural relaxation and other processes involved in dynamics of excited states. The scope of the approach we have developed is presented for the example of the $Na_2F$ molecule. This is the smallest prototype of $Na_nF_{n-1}$ clusters with a single excess electron for which the calculation of the *first excited state* is particularly simple and therefore suitable for developing and testing new approaches to ultrafast dynamics of clusters. This work was motivated by the stationary spectroscopical properties of $Na_nF_{n-1}$ clusters which are characterized by a dominant infrared transition arising from the excitation of the single excess electron from the ground state to the first excited state [3]. Since the dominant infrared transition is well separated, an adia-

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batic approach to the dynamics of the first excited state is suitable.

## 2 Methodology

For systems such as alkali–halide clusters with a single excess electron, the correlation energies of the ground and excited states are comparable due to the strong ionic bonding and therefore, the correlation contributions to the transition energies can be neglected without introducing considerable errors. Moreover, the relaxation of the doubly occupied MO's due to the excitation of the excess electron can be also neglected. We tested the validity of the approximations by comparing the stationary absorption spectra obtained from this approach with MCLR and CI calculations and found excellent agreement [4]. In other words, ground state MO's can be used for building the following one-electron effective Hamiltonian for the system

$$h'_{ij}(\mathbf{R}(t)) = h_{ij}(\mathbf{R}(t)) + \sum_{c}^{d.o.} [2(ij|cc) - (ic|cj)] \qquad i, j = o, ..., M \tag{1}$$

where the MO indices $i, j$ run over the singly occupied and virtual orbitals only ($o$ denotes the open shell HOMO and $M$ is the size of the basis) while the sum extends over all doubly occupied orbitals. We used the standard quantumchemical notation $(ij|cc)$ and $(ic|cj)$ for the Coulomb- and exchange integrals, respectively. The energies of the excess electron, denoted by $\varepsilon'_i$, are then obtained by the diagonalization of the Hamiltonian (1). In the classical approximation, the motion of the nuclei is governed by the Newtonian equations

$$m\ddot{\mathbf{R}} = -\nabla_R E_i(\mathbf{R}(t)) \tag{2}$$

where $E_i(\mathbf{R})$ is the molecular total energy in the state $i$. Since we are interested in the dynamics in one particular excited state $i$, within our approach the total energy is given by

$$E_i(\mathbf{R}(t)) = E_{\mathrm{nuc}} + E^{\mathrm{HF}} - \varepsilon'_o + \varepsilon'_i. \tag{3}$$

where $E_{\mathrm{nuc}}$ is the Coulomb energy of the nuclei, $E^{\mathrm{HF}}$ is the Hartree–Fock electronic energy and $\varepsilon'_o$ is the lowest eigenvalue of the effective Hamiltonian.

In order to simulate the nuclear dynamics of the system according to (2), we need to calculate the gradients of the energy contributions in (3). The gradients of $E_{\mathrm{nuc}}$ and $E^{\mathrm{HF}}$ are well–known [5]. The gradients of the eigenvalues of the effective Hamiltonian $\frac{\mathrm{d}\,\varepsilon'_i}{\mathrm{d}\mathbf{R}_a}$ involve besides the derivatives of the one- and two-electron integrals also the response of the MO coefficients $c^i_\mu$ with respect to the nuclear displacements $\frac{\partial c^i_\mu}{\partial \mathbf{R}_a} = \sum_m^{\mathrm{MO}} U^a_{\mathrm{mi}}\, c^m_\mu$, where, in general, the $U$ matrices contain elements for which the corresponding orbital transformations either change the Hartree–Fock energy or only canonicalize the MO's. Since the MO coefficients in our approach are those of the restricted open shell Hartree–Fock (ROHF), the $U$ matrices have to be obtained from the solution of the coupled perturbed Hartree–Fock equations (CPHF) for the open shell RHF, cf. [6]. Usually, in quantum chemistry the CPHF equations are needed as an intermediate step for the analytic computation of the vibrational frequencies. Obviously, for this aim only those $U$ matrix elements are required for which the corresponding orbital transformations do change the HF energy. For our purpose, however, the calculation of the derivatives of $\varepsilon'_i$ requires the knowledge of all $U$ matrix elements, including those ones corresponding to the canonicalization of the MO's [7]. Therefore, we used the formulation and efficient implementation of the *extended* CPHF equations due to Rice *et al.* [8] and Lee *et al.* [9] which yields all $U$ matrix elements as a solution of a system of linear equations.

Summarizing, the calculation of the electronic energies from (1) and the solution of Newton's equation of motion (2) for the nuclei together with the solution of the extended CPHF equations allow the simulation of the adiabatic molecular dynamics in an electronically excited state in the framework of the above described model.

In this contribution we are interested in the simulation of pump–probe signals for the ground state-to first excited state-to positive ion spectroscopy. In this spectroscopy, a thermal ensemble of clusters is initially prepared in the electronic ground state. Excitation by the pump pulse generates a phase space occupation on the first excited electronic state whose dynamics is monitored by a second, time delayed probe pulse ionizing the molecule. In analogy to [1], the simulation of the pump–probe signal can be carried out by utilizing the Wigner representation of the density matrix. Moreover, the perturbation expansion up to the first order in the pump and the probe fields is used. Notice that in the Wigner representation the coordinates of the nuclei $\mathbf{R}(t)$ used in (1) to (3) are transformed into the center of mass coordinates $\mathbf{q}$ and the relative coordinates. The Fourier transform of the latter leads to the definition of the classical momentum $\mathbf{p}$ (for details cf. [1]). Within this approach, the pump–probe signal is given by

$$\begin{aligned} S[t_{\mathrm{d}}] \sim \int \mathrm{d}\mathbf{q}_0\, \mathrm{d}\mathbf{p}_0 \int_0^\infty \mathrm{d}\tau_1 \exp\left\{ -\frac{(\tau_1 - t_{\mathrm{d}})^2}{\sigma_{\mathrm{pu}}^2 + \sigma_{\mathrm{pr}}^2} \right\} \\ \times \exp\left\{ -\frac{\sigma_{\mathrm{pr}}^2}{\hbar^2} [E_{\mathrm{pr}} - V_{1,+1}(\mathbf{q}_1(\tau_1; \mathbf{q}_0))]^2 \right\} \\ \times \exp\left\{ -\frac{\sigma_{\mathrm{pu}}^2}{\hbar^2} [E_{\mathrm{pu}} - V_{1,0}(\mathbf{q}_0)]^2 \right\} P_{00}(\mathbf{q}_0, \mathbf{p}_0), \end{aligned} \tag{4}$$

where $P_{00}(\mathbf{q}_0, \mathbf{p}_0)$ is the initial Wigner distribution on the electronic ground state. $V_{1,0}$ and $V_{1,+1}$ denote the energy gaps between the first excited state and the ground state, and between the cationic ground state and the first excited state, respectively. The quantities $\sigma_{\mathrm{pu,pr}}$ and $E_{\mathrm{pu,pr}}$ are the pulse durations and excitation energies of the pump and the probe, respectively, and $t_{\mathrm{d}}$ is the time delay. Based on (4), the following picture of the pump–probe excitation can be given: At the beginning the molecule is prepared in the electronic ground state 0 represented by the Wigner distribution function $P_{00}(\mathbf{q}_0, \mathbf{p}_0)$ in the classical phase space constituted by coordinates $\mathbf{q}_0$ and momenta $\mathbf{p}_0$. This initial phase space density is spectrally filtered during the pump process to the first excited state 1 by the third Gaussian of (4). Subsequently, the filtered ensemble evolves on the first excited state and is spectrally filtered again during the delayed probe pulse (given by the second Gaussian of (4)) ionizing the molecule. The evolution of the ensemble is performed by propagating classical trajectories along the first excited electronic state as described above. The final time resolution of the signal is determined by the pump–probe correlation function given by the first Gaussian of (4).

## 3 Initial conditions

The equilibrium structure in the electronic ground state of $Na_2F$ is the triangular geometry ($r_1(\mathrm{Na{-}F}) = 1.93$ Å, $r_2(\mathrm{Na{-}Na}) = 3.01$ Å, $\alpha(\mathrm{Na{-}F{-}Na}) = 102.5°$, cf. [10]).

We started the simulation by generating a phase space density in the ground state of $Na_2F$ for a initial vibrational temperature of 50 K. The phase space density of the molecule at this temperature is represented by an ensemble of both 300 coordinates and momenta, which were obtained by sampling the Wigner distribution function of a canonical ensemble with respect to $\mathbf{q}_0$ and $\mathbf{p}_0$ [11]:

$$P_w(\mathbf{q}_0, \mathbf{p}_0) = \frac{1}{\pi\hbar} \prod_i \tanh\left(\frac{\hbar\omega_i}{2k_\mathrm{B}T}\right) \times \exp\left[-\frac{2}{\hbar\omega_i}(\mathbf{p}_0^2 + \omega_i^2 \mathbf{q}_0^2) \tanh\left(\frac{\hbar\omega_i}{2k_\mathrm{B}T}\right)\right], \quad (5)$$

where $\omega_i$ are the frequencies of the normal modes of the molecule and $\prod_i$ denotes the product over all normal modes. For finite temperatures, the equilibrium triangular structure of the molecule is slightly distorted by the thermal motions. These can be characterized by the abundance of the energy gaps between the ground and first excited state of $Na_2F$ (cf. Fig. 1). The energy gaps are centered around 1.05 eV which corresponds to the value calculated at the equilibrium triangular geometry of $Na_2F$.

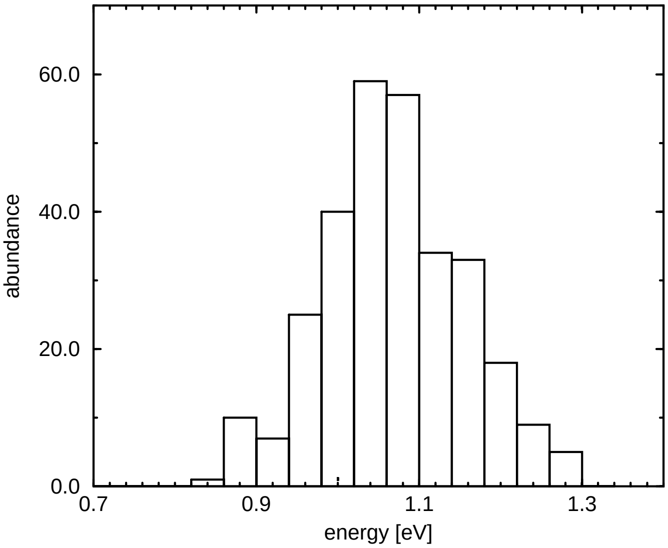

**Fig. 1.** Histogram of the energy gaps between the first excited and the neutral state of a 50 K initial ensemble of $Na_2F$.

## 4 Excited state dynamics of $Na_2F$

Starting from the initial ensemble corresponding to the triangular geometry, the vertical transition initiated by the pump pulse creates a phase space density on the first excited electronic state of $Na_2F$. Due to the bond breaking between the sodium atoms, the equilibrium geometry of the first excited electronic state is linear ($r(\mathrm{Na{-}F}) = 1.96$ Å). As a consequence, the molecule has a large vibrational excess energy (0.5 eV) and starts to relax.

We have investigated the dynamics of the system by propagating 300 trajectories on the first excited electronic state, with the ensemble of 300 sampled phase space points as the initial conditions. Information on the timescales of the relaxation process can be obtained by analyzing the time resolved dynamics in terms of the averaged bond angle between the fluorine and the two sodium atoms. It was obtained by determining the Na–F–Na bond angle for each trajectory separately and then averaging over the entire ensemble of trajectories. As can be seen from Fig. 2a, the averaged bond angle shows regular oscillations between 100 and 180 degree with a period of 180 fs corresponding to a bent-to-linear structural relaxation. The period of the oscillation is equal to half the vibrational period of the bending mode due to the equivalence of the bending in both directions. In Fig. 2b, the root mean square displacements (rms) of the averaged bond angle are shown during the relaxation dynamics of the molecule. Their values oscillate as well as the averaged bond angle itself and remain smaller than 20 degrees over the entire propagation time of 2 ps. From this behaviour we conclude that the dynamics remains concerted and processes of intra molecular vibrational relaxation (IVR) are not pronounced up to the propagation time of 2 ps. Moreover, we investigated the long-time behaviour of the dynamics by propagating a trajectory up to 15 ps. Also in this case, no significant IVR could be detected. Such behaviour for the *excited state dynamics* of $Na_2F$ is in contrast to the result for the *ground state dynamics* of $Ag_3$ where no bond breaking between any of the atoms occurs. In the latter case, an intracluster collision of two terminal silver atoms takes place at about 1 ps which triggers the onset of IVR from the bending to the symmetric stretch coordinate [1].

Next we have investigated the time evolution of the energy gaps between the cationic and first excited neutral state for each trajectory, $V_{1,+1}$, which are the central quantities for the simulation of the pump–probe signal (cf. (4)). For the illustration, we have build the time-dependent averaged energy gap by extracting the energy gaps along each of the 300 trajectories separately, and af-

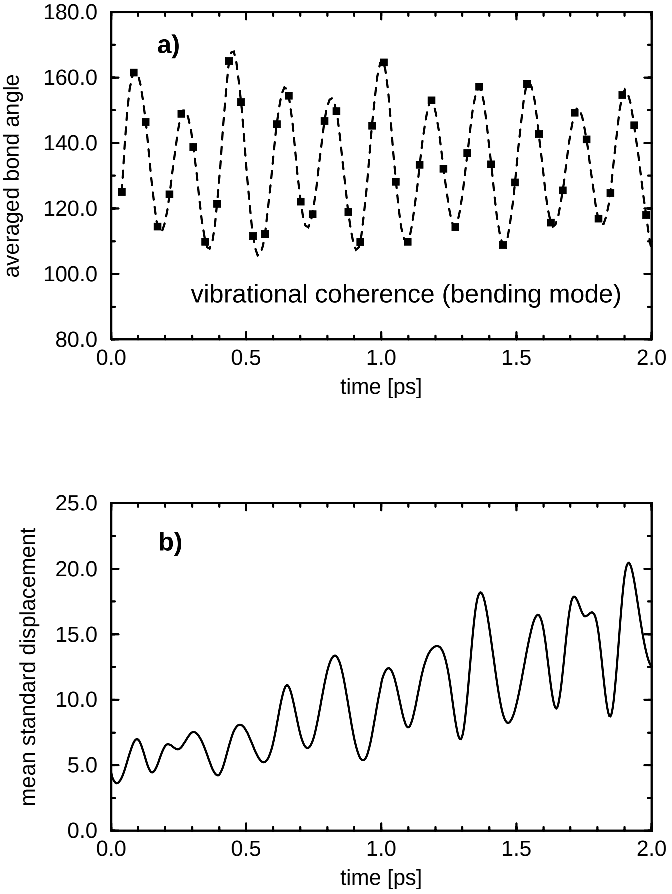

**Fig. 2.** (a) Squares: The time evolution of the averaged bond angle for the first excited state dynamics of Na$_2$F for a 50 K initial ensemble, the dashed line is only to guide the eye; (b) Root mean square displacement of the averaged bond angle.

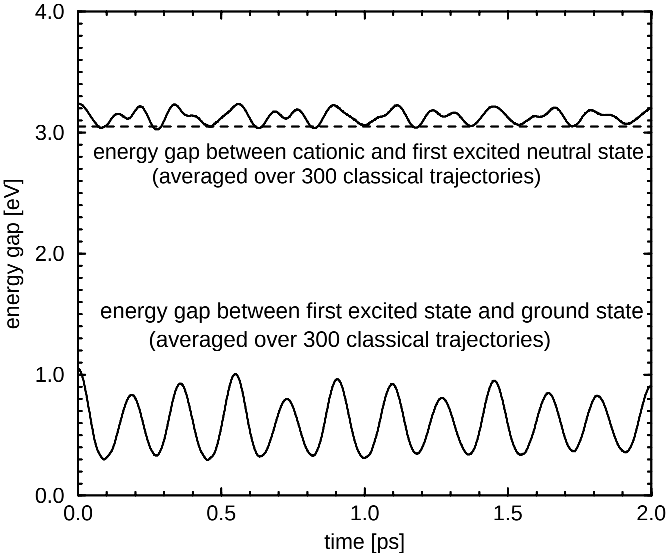

**Fig. 3.** Time–dependent averaged energy gaps for the first excited state dynamics of Na$_2$F for a 50 K initial ensemble, dashed line marks the excitation energy of the probe laser in the pump–probe simulation (cf. Fig. 4).

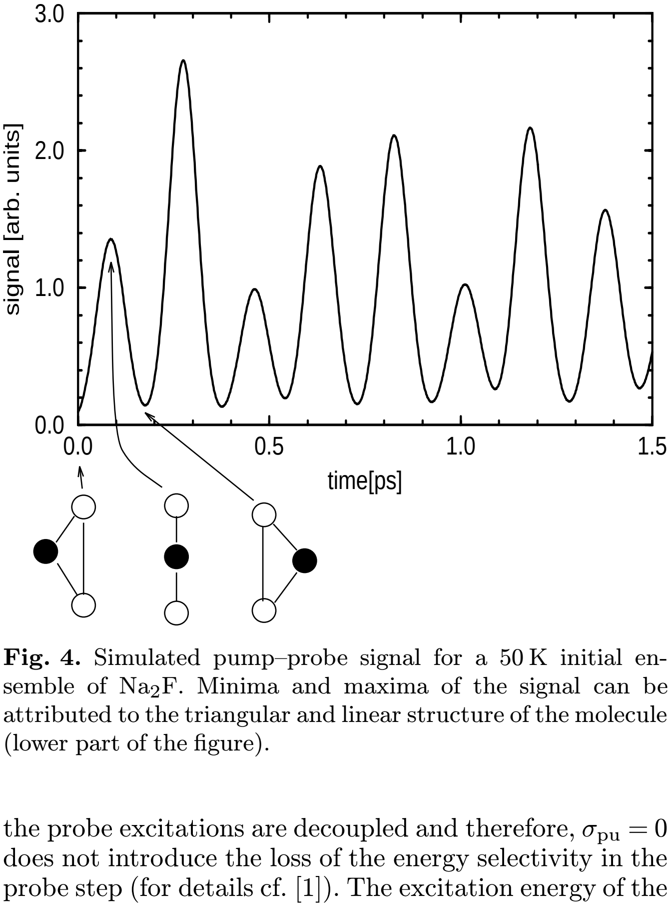

**Fig. 4.** Simulated pump–probe signal for a 50 K initial ensemble of Na$_2$F. Minima and maxima of the signal can be attributed to the triangular and linear structure of the molecule (lower part of the figure).

terwards averaging over the entire ensemble. As can be seen from the upper part of Fig. 3, the energy gap mainly oscillates with the period of the Na–F–Na averaged bond angle between an energy interval of 3.03 eV (409 nm) up to 3.25 eV (381 nm) providing the information for experimentalists on the wavelength of the probe laser. Furthermore, in the lower part of Fig. 3 the time dependent averaged energy gap between the first excited electronic state and the ground state is shown. The regular oscillations have a period corresponding to the period of the Na–F–Na averaged bond angle and cover an energy range of 0.3 eV (4133 nm) up to 1.05 eV (1181 nm). This information may be of interest in pump–dump experiments.

Figure 4 shows the simulated pump–probe signals (cf. (4)) for the ensemble with 50 K initial temperature. In the present study we considered zero pump pulse duration ($\sigma_{\mathrm{pu}} = 0$). In this case, the third exponential in (4)) is equal to unity and therefore, the spectral filtering (initial condition selection) is disregarded. Thus the entire ground state ensemble prepared at the given temperature is excited by the pump which enables us to obtain the comprehensive information on the dynamics in the first excited electronic state of Na$_2$F. Notice, that due to the perturbation expansion with respect to the fields used in (4), the pump- and the probe excitations are decoupled and therefore, $\sigma_{\mathrm{pu}} = 0$ does not introduce the loss of the energy selectivity in the probe step (for details cf. [1]). The excitation energy of the probe laser, $E_{\mathrm{pr}} = 3.05$ eV (406 nm), was chosen to be resonant with the minima of the averaged energy gaps between the cationic and first excited neutral state (cf. the dashed line of Fig. 3). As can be seen by comparing Figs. 3 and 2a, the minima of the energy gaps correspond to the linear geometry of the molecule, and therefore, the pump–probe signal provides information on the structural relaxation of $Na_2F$ in the first excited electronic state. A probe pulse duration of $\sigma_{\mathrm{pr}} = 50\,\mathrm{fs}$ was chosen in order to be able to time resolve the oscillations in the Na−F−Na averaged bond angle (period of 180 fs). As expected, the pump–probe signal (Fig. 4) shows vibrational coherence reflecting the bent-to linear-to bent structural relaxation (lower part of Fig. 4), and no features of IVR can be detected which would show up in a broadening of the signal and/or vanishing of the regular oscillatory feature. Again, this is in contrast to the ground state dynamics of $Ag_3$ where the processes of IVR are mirrored in the signal after the intracluster collision of two terminal silver atoms occuring at about 1 ps.

In conclusion, we have shown that the combination of ab–initio quantumchemical methods and the Wigner distribution approach allows for the investigation of the excited state dynamics of alkali–halides with a single excess electron. In the particular test example of the $Na_2F$ molecule we found that the pump–pulse induced excitation of the first excited state of $Na_2F$ leads to a bond breaking of the Na atoms and a subsequent motion of the molecule along the bending coordinate from the triangular to the linear structure (in the framework of quantum mechanics this would correspond to a coherent motion). The corresponding simulated pump–probe signal shows strong effects of vibrational coherence and no features of intra molecular vibrational relaxation could be detected.

The study of larger alkali–halides with a single excess electron such as $Na_3F_2$, $Na_4F_3$ and $Na_5F_4$ is in progress. In particular we will investigate the nature of excited states and the dynamics of localized excitations in these clusters which are characterized by (i) lattice defects ($Na_4F_3$) and (ii) an atom attached to either a planar ionic subunit ($Na_3F_2$) or a cuboidal structure ($Na_5F_4$) [3].

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