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Energy distribution of H^- ions produced by double capture in proton-H_2 collisions

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The distribution of excitation energy for the $H_2(v=0,j=0,1)\rightarrow H_2{}^{2+}$ process has been measured by the technique of double charge transfer, and is compared with the results of a Franck-Condon calculation. It is shown that this calculation accurately describes double ionization of H_2 by charge transfer apart from a small scale shift.

INTRODUCTION

Double ionization of H_2, either by electron impact[1] or fast H^+ and D^+ projectiles[2–4] has been studied since 1930.[5] This interest is justified by the simplicity of this two-electron system; it is the simplest candidate for testing collision theories and serves as a model for studying molecular double ionization. This process is particularly attractive to study because the potential surfaces of $H_2{}^+$ and $H_3{}^+$ are well known, and consequently it might be expected that theoretical calculations can be carried out. The Franck-Condon principle has been applied to vertical ionization processes since the beginning of "modern molecular physics."[6] However, transition to a dissociative state can also be considered as the limiting case of rovibronic excitation as shown in electron— or ion—diatomic-molecule collisions.[7] The question arises whether the target can be considered as a point-mass scatterer or as two distinct atoms which interact individually with the projectile during the collision.[8] Also, it is questionable whether the collision should be treated in the frame of the molecular-orbital model,[9] which assumes that the partners of the colliding system form a quasimolecule during the collision.

The answers to these questions are not straightforward, and certainly depend on collision energy. It is generally admitted that the Franck-Condon principle fails when the collision velocity is lower than the velocity of electrons in their molecular orbitals. However, even in such a case it is not clear that this principle fails because it may be applied to the quasimolecular system, distorted by the interaction with the incoming projectile.

The first theoretical and experimental test of double ionization of H_2 was given by McCulloh and Rosenstock,[1] using 0.5—1-keV electrons. By a coincidence technique they measured the kinetic energy distribution of the proton pair. Experimental data were compared to the Franck-Condon (FC) overlap between the H_2 ground state and the $H_2{}^{2+}$ continuum state. The conclusion of this work was consistent with a direct two-electron ejection mechanism for double ionization of molecular hydrogen. The kinetic energy spectra of fragments produced from $H_2{}^{2+}$ and $D_2{}^{2+}$ during the bombardment of H_2 and D_2 by 0.5—4-MeV H^+, $H_2{}^+$, He^+, and O^+ projectiles were also obtained by Edwards, Wood, and Steuer.[10,11] Since the data were obtained by time-of-flight and energy measurements not in coincidence, all dissociative channels were observed together. The reflection approximation[12] was used to predict the spectra of H^+ coming from the dissociative $2p\ \pi_u$, $2s\ \sigma_g$, and $2p\ \sigma_u$ states of $H_2{}^+$ and from doubly ionized H_2. The experimental results were correctly reproduced by adding a supplementary electronic transition to an autoionizing state of $H_2{}^+$.

More recently, the double-ionization cross section of thermal H_2 by 0.1—4-MeV H^+, D^+, or He^+ projectiles has been studied by Edwards, Wood, and Ezell.[2–4] The electronic transition to the double-ionized state was identified by observing in coincidence the two protons, and this for the internuclear axis of H_2 oriented at approximately 90° and 30° relative to the ion-beam direction. It was shown that Bethe theory does not give even a qualitative agreement with the experimental results. In the 0.1—1-MeV collision-energy range these experimental data were well fitted by an impact-parameter calculation,[4] and it was concluded that excitation occurs through a two-step model, where the double ionization is induced by two independent interactions between the electron and the projectile rather than through a shake-off process.

In the present work, we focus our attention on one particular process of double ionization of H_2, where the two electrons are not ejected into the continuum state but rather attach to the projectile. Namely, we have studied the following double-charge-transfer reaction:

$$H^+ + H_2 \rightarrow H^- + H_2{}^{2+} .$$

This experiment deals with low-keV-energy collisions near zero scattering angle. From the H^- kinetic energy distribution, we have deduced the amount of translational energy used for the electron transfer $H_2\rightarrow H_2{}^{2+}$ transition, and consequently the c.m. kinetic energy distribution for the proton pair. This work is also a sensitive test of the double-charge-transfer technique, pioneered in 1972,[13] for double-ionization energy measurements.

The study of doubly charged molecules is presently the subject of many theoretical and experimental investigations.[14–16] In fact, the high density of electronic states of these species makes it difficult to perform accurate calculations. On the other hand, various techniques are available for the determination of these states. Laser photodissociation[17] can be used in special cases to achieve high-resolution spectroscopy of bound and quasibound states. More generally, Auger spectroscopy[18] is the most powerful tool for achieving medium resolution. In charge-stripping experiments,[19] the internal energy of long-lived cations is determined with an accuracy of 0.5 eV. Another method uses uv light as the ionization radiation together with ion-fragment coincidence measurements of the kinetic energy released after fragmentation of the ions to estimate the energy level of double charged precursor states.[16]

Measurement by translational spectroscopy of the kinetic energies of H^- ions arising from double charge transfer of H^+ provides a complementary technique which can determine the energies of doubly charged states with at least comparable precision provided that the transitions obey the FC principle.

We have repeated the previous work of Fournier *et al.*[20] with a better energy resolution and improved signal-to-noise ratio, using both H_2 and D_2 as targets. Considering their lightness, these two molecules are the worst candidates for FC transitions, and consequently the best trials for the capability of the technique.

APPARATUS AND EXPERIMENTAL METHOD

The apparatus used is a double mass spectrometer. After mass analysis by a Wien filter of resolution 300, a proton beam is defined by two collimating holes of 30 μm diameter placed 20 cm apart. The H^- beam produced by collisions with the gas target is first angularly determinated by a 30-μm-diam diaphragm, at 20 cm from the collision chamber. It is energy analyzed by an electrostatic deflector of resolution 5000. The signal is detected by a channel-electron multiplier and the data recorded on a multichannel analyzer.[14] From the measurement of the kinetic energy of the H^- ions produced by collision of monoenergetic protons with the molecule target, one can determine the energy of simple ionization and double ionization of the target.

For instance, for the collision $H^+ + H_2 \rightarrow H^- + H_2{}^{2+}$ the double-ionization potential is given by

$$I^{2+} = T - T_0 - T_m - E(H^-) ,$$

where T_0 and T are, respectively, the initial H^+ and final H^- kinetic energy in the laboratory frame, $E(H^-)$ is 14.3 eV, the energy of the fundamental state of H^- relative to H^+ [only this state is taken into account, the short lifetime of the excited state of H^- (Ref. 21) does not allow them to reach the electrostatic analyzer]. T_m is the recoil energy (10 meV), negligible considering our experimental conditions.

H^- can also be produced by successive simple charge transfer:

$$H^+ + H_2 \rightarrow H + H_2{}^+(1) ,$$

$$H + H_2 \rightarrow H^- + H_2{}^+(2) .$$

In this case the ionization potentials are

$$I^+(H^+(1)) + I^+(H^+(2)) = T - T_0 - E(H^-) ,$$

where $H_2{}^+(1)$ and $H_2{}^+(2)$ indicate two different electronic states. The intensity of the H^- beam produced by collisions is linear with the pressure of the gas target in the case of direct double ionization and is quadratic in the case of successive simple ionization. This enables us to differentiate the two processes.

RESULTS

This method requires a calibration in energy which is done by collisions with a noble gas of well-known double-ionization energy.[14,22] Figure 1(a) shows an energy spectrum of H^- obtained by collisions of 9-keV protons with argon. The first peak *A*, whose intensity is quadratic with the pressure of the target, is an overlap of three possible transitions to ${}^2P_{3/2}, {}^2P_{1/2}$ states of Ar^+.[23] We find for this peak a mean value of 31.68 eV. The second peak *B*, linear in intensity with the pressure, is attributed to formation of Ar^{2+} in the ${}^1D_2$ state by double ionization and is estimated to be at 45.12±0.2 eV. We notice in this spectrum that transition to ${}^3P$ and ${}^1S_0$ states of Ar^{2+} is not observed. Figures 1(b) and 1(c) are energy-loss spectra of H^- produced by collision of protons with an H_2 target at pressures of 10^{-4} and 10^{-5} Torr, respectively. The kinetic energy of the collision is 9 keV. Three peaks appear at higher pressure (10^{-4} Torr). The first peak *A*, located

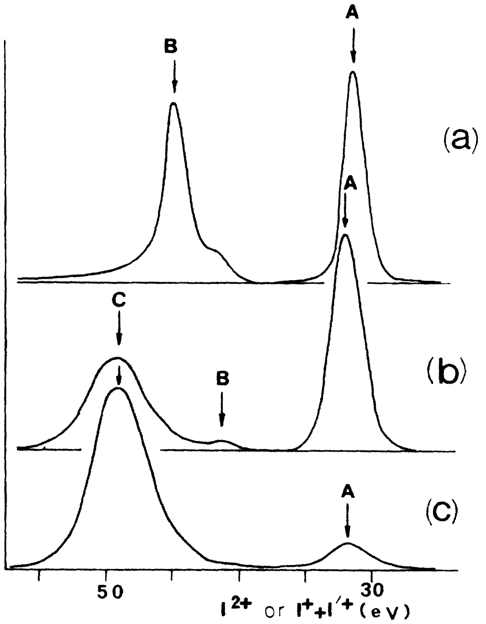

FIG. 1. (a) Translational energy spectra of H^- ions from 9-keV H^+ impinging on Ar. (b) and (c) Pressure effect on translational energy spectra of H^- ions impinging on H_2 at 9 keV: (b) high pressure (10^{-4} Torr), (c) low pressure (10^{-5} Torr).

at 31.8 eV [2.9 eV full width at half maximum (FWHM)], is the result of a two-step ionization of the gas target to the fundamental state $1s\ \sigma_g$ of H_2^+ with the most probable vibrational state $v=4$. This is in agreement with the FC principle applied to direct simple ionization.[24] The lower limit of the peak corresponds to twice the energy needed for the formation of $H_2^+(v=0)$ whereas the upper limit is related to ionization to the dissociative continuum of the $1s\ \sigma_g$ state of H_2^+. The peak *B*, at 10.2 eV from the peak *A*, corresponds to excitation of the projectile to the state H(2*p*) (Ref. 25) which emits a Lyman-α radiation before the second collision which produces H$^-$.

In the present experiment, the target density was maintained at a factor of 10 lower than in previous work,[20] Fig. 1(c). Under these conditions the intensity of peak *C*

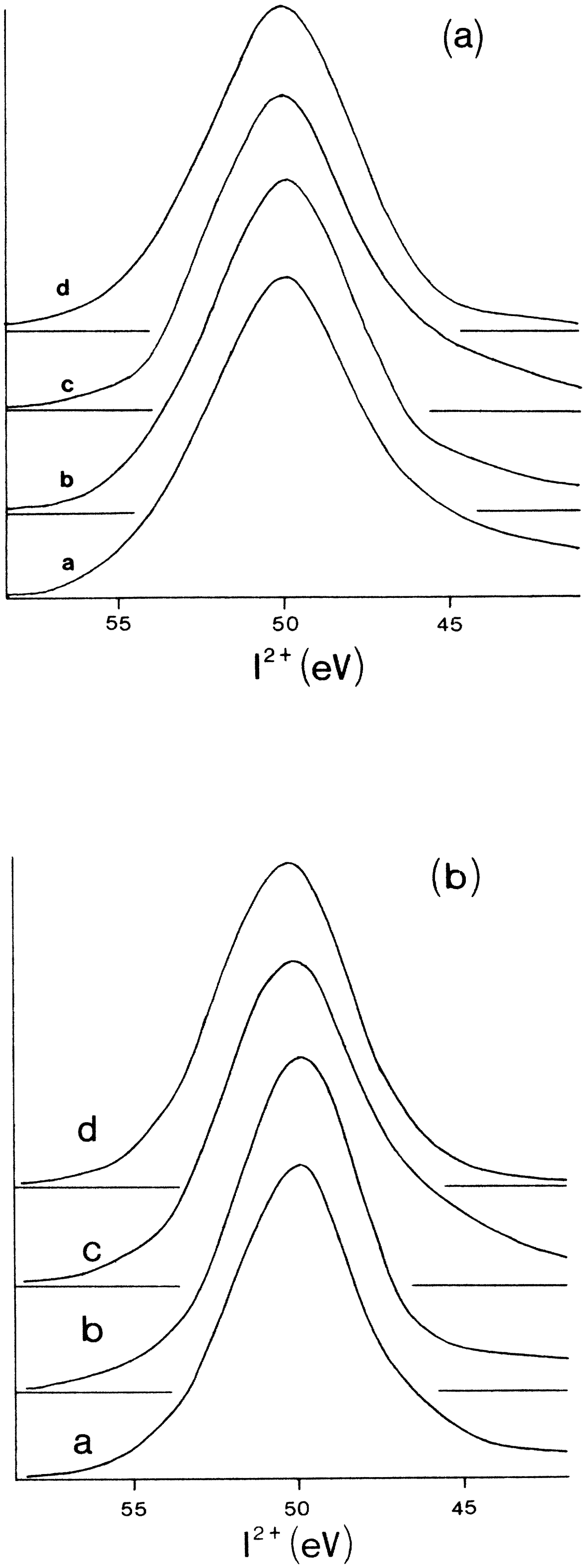

FIG. 2. $F(I^{2+})$ distribution obtained via a spline fit of the experimental data of the double-ionization energy I^{2+} of (a) H_2 and (b) D_2, measured at low pressure and for collision energies of, curve *a*, 3 keV; *b*, 5 keV; *c*, 7 keV; and *d*, 9 keV.

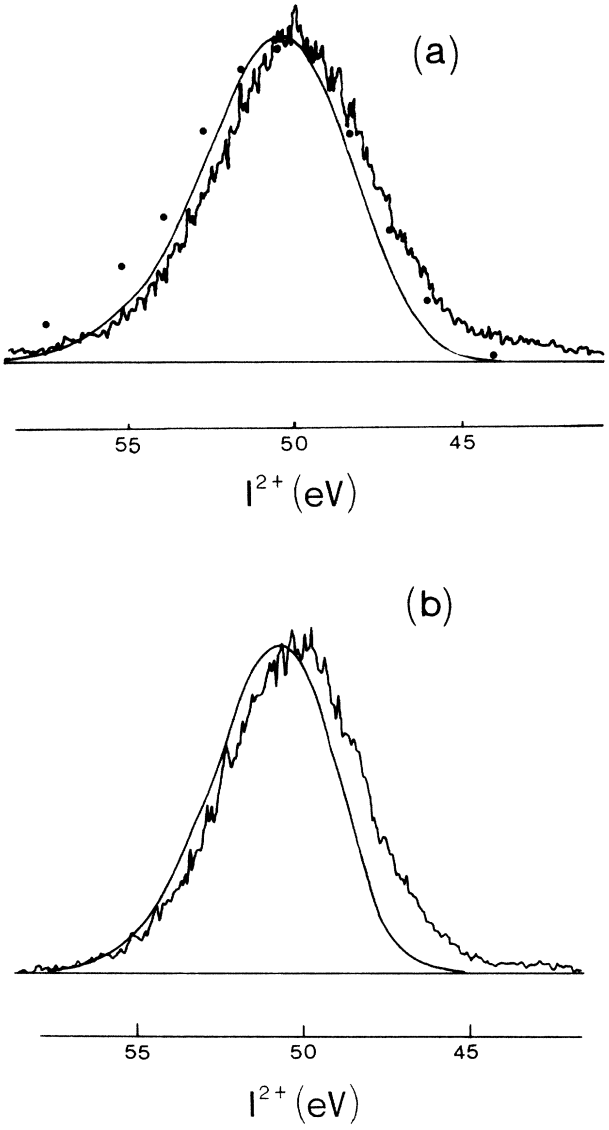

FIG. 3. Comparison of $F(I^{2+})$ distribution of the double-ionization energy I^{2+} and the Franck-Condon calculation for (a) H_2 at 9 keV. [The points are the electronic-impact experiment (from Ref. 1)] and (b) D_2 at 9 keV.

TABLE I. Double-ionization energy I^{2+} and FWHM (ΔE) measured for H_2 and D_2, with an uncertainty of 0.3 eV. T_0 and $E_{\text{c.m.}}$ are the collision energies in the laboratory and in the center-of-mass frame. Calculated values of I^{2+} and FWHM (ΔE) are, respectively, 50.4 and 5.3 eV for H_2, and 50.6 and 4.3 eV for D_2.

T_0 (eV)	$E_{\text{c.m.}}(H_2)$ (eV)	$I^{2+}(H_2)$ (eV)	$\Delta E(H_2)$ (eV)	$E_{\text{c.m.}}(D_2)$ (eV)	$I^{2+}(D_2)$ (eV)	$\Delta E(D_2)$ (eV)
3000	2000	49.3	5.1	2400	49.8	4.1
5000	3333	49.4	5.0	4000	49.9	4.2
7000	4666	49.5	5.3	5600	49.9	4.2
9000	6000	49.6	5.1	7200	50.2	4.3

is linear with increasing pressure of the target and its energy distribution does not contain contributions from the two-step collision processes.[20]

To get a high-energy resolution, it is necessary to detect only those H^- ions emitted at very small laboratory scattering angles. In the present case, the angular spread is about $\pm 10^{-4}$ rad. This leads to an "apparent" cross section which represents a small fraction of the total cross section. True total cross sections have been already measured, both for the two-step process $H^+ \rightarrow H$ (the cross section is $\sigma = 8.55 \times 10^{-16}$ cm^2, Williams and Dunbar[26]), $H \rightarrow H^-$ ($\sigma = 2.4 \times 10^{-17}$ cm^2, Williams[27]); and for the direct double-capture process $H^+ \rightarrow H^-$ ($\sigma = 2.76 \times 10^{-18}$ cm^2, McClure[28]). From the present counting rates obtained for double-capture H^- ions, one can estimate the apparent double-capture cross section to be about 3×10^{-22} cm^2, which represents only a fraction of 10^{-4} of the true total one. It corresponds actually to a quasi-zero differential cross section of about 10^{-16} cm^2/srd. More generally, in the present experiment, any process is observed at very small scattering angles, i.e., at large impact parameters.

The amount of the energy needed for the H_2 to $H_2{}^{2+}$ transition was measured experimentally for collision energy ranging from 3 to 9 keV. Results are reported in Fig. 2(a). Each spectrum corresponds to a 10-h scan. Similar studies for the D_2 to $D_2{}^{2+}$ transition are reported in Fig. 2(b).

Taking into account the experimental resolution of the apparatus, we have deduced the widths of the $H_2{}^{2+}$ and $D_2{}^{2+}$ states reached during the collision; ionization energies and widths are given in Table I.

DISCUSSION

We have tried to interpet this energy distribution in terms of Franck-Condon vertical electronic transitions from H_2 to $H_2{}^+$. Theoretical distributions are given by the well-known formula

$$F(E) = \rho(E) \,|\, \langle X_e(R) X_v(R) \rangle \,|^2 ,$$

where $\rho(E) = (2\mu h)^{-1}(2/W)^{1/2}$ is the state density in the dissociation continuum of $H_2{}^{2+}$, and μ is the H_2 or D_2 reduced mass. W is the c.m. kinetic energy of the $H^+ + H^+$ fragments for a given electronic transition. The vibrational wave function $X_v(R)$ for $H_2(v=0, j=1)$ is space normalized, and the amplitude of the continuum wave function $X_e(R)$ is taken equal to 1 for large values of the internuclear distance. Numerical values of the $(1s\ \sigma)^2$ potential are taken from Sharp.[29]

The $H_2{}^{2+}$ potential is pure Coulombic ($1/R$, in a.u.). Results of the calculation are illustrated in Figs. 3(a) and 3(b). For H_2 the most probable value of I^{2+} is 50.4 eV and the distribution of I^{2+} extends from 45 to 59.3 eV with an FWHM of 5.3 eV. For D_2 the maximum in the distribution is around 50.6 eV and the FWHM is smaller, i.e., 4.3 eV. A straightforward application of the reflection method gives values of I^{2+} of 51.3 and 51.4 eV, respectively, for H_2 and D_2. The sharpening of the $D_2{}^{2+}$ distribution is due to the lowering of the $v=0$, $j=0,1$ rovibrational levels.

The translational energy spectra of H^- recorded in this experiment were obtained for target pressures 1 order of magnitude lower than in Ref. 20. Also, with the collision chamber electrically isolated, and at a potential different from ground, it was possible to remove entirely the scattering signal due to collisions with residual gas outside the collision cell. Under such conditions, the distributions of Figs. 3(a) and 3(b) are directly the $H_2 \rightarrow H_2{}^{2+}$ and $D_2 \rightarrow D_2{}^{2+}$ energy distributions $f(I^{2+})$, and the data are not altered by the double-collision process.[20] These distributions remain almost invariant for collision energies varying from 3 to 9 keV. They are almost identical when we take into account apparatus effects. The experimental broadening is due to (i) the initial energy distribution of H^+ formed in the ion source through an electron-impact dissociative collision $1s\ \sigma_g \rightarrow 2p\ \sigma_u$ (0.4 eV), and (ii) the energy resolution of the electrostatic analyzer. The corrected experimental FWHM (ΔE) of the distributions is given in Table I. We notice a small change, close to the margin of error, in the most probable value of double-ionization energy, from 49.3 to 49.6 eV for H_2 and from 49.8 to 50.2 eV for D_2, when the collision energy increases from 3 to 9 keV.

In this energy domain, the H^- signal increases strongly, quasiexponentially with the incident energy, in agreement with previous studies.[28] The cross section for charge transfer $H^+ + H_2 \rightarrow H^-$ has been studied for energies between 10^2 and 10^6 eV and it has a sharp maximum of 10^{-17} cm^2 around 20 keV. The experimental and theoretical H^- energies at 9 keV are compared in Fig. 3(a) to the H^+-H^+ ion-pair kinetic energy distribution $f(W)$, obtained by 0.5- and 1-keV electron impact (1): It may be noticed that the distribution $f(I^{2+})$ of the double-ionization energy I^{2+} measured in our experiment is simply related to the distribution $f(W)$ of the fragment c.m. kinetic energy W by

$$F(I^{2+})=f(W=I^{2+}-D-2I_{\infty}{}^{+})\ ,$$

where D is the dissociation energy of $H_2(v=0,j=1)$ and $I_{\infty}{}^{+}$ is the ionization energy of H(1s).

The broadening of electron-impact spectra (1) is explained by the experimental sampling function. The maximum of the electron-impact experimental distribution is between $I^{2+}=51$ and 49 eV, while the maximum is around 49.6 ∓ 0.2 eV in our experiment. In the electron energy range 0.5–1 keV, no change in the distribution is noticed, as it is in our work.

By time-of-flight and energy-analysis techniques,[11] the H^+ yield from double ionization induced by proton impact was found to be very low and measurements were obtained only for 1 MeV. Meanwhile He^+ and O^+ projectiles produce appreciable double ionization, which decreases exponentially when the beam velocity increases. The experimental energy distribution was centered around 50.12 eV and the width was about 6.4 eV.

The predicted energy distribution for $H_2{}^{2+}$ production calculated by Edwards *et al.*[2] within the reflection approximation is centered around $I^{2+}=51$ eV, with a FWHM of 6.3 eV. However, McCulloh,[30] using a Morse potential for H_2, has already shown that an exact quantum calculation differs from the reflection approximation.[12,31] In our quantal calculation, an exact H_2 potential is used. The result is in agreement within 0.1 eV with McCulloh ($I^{2+}=50.27$ eV and the FWHM is 5.1 eV).

As it can be seen in Figs. 3(a) and 3(b), the experimental distributions for H_2 and D_2, including instrumental effects, are remarkably close in shape to the theoretical distribution. However, a systematical energy shift of about 0.7 eV remains. It seems to decrease when the collision energy increases. This small discrepancy corresponds to a shortening of the H_2 internuclear distance of about 0.05 Å.

CONCLUSION

In the domain of collision energy, lying from 3 to 9 keV, a small deviation was observed from Franck-Condon transition probabilities. However, there was no need to invoke any sequential $H_2{}^+$ excitation, as referred to in a recent work.[4] This can be explained by the fact that this latter work, performed at much higher collision energies (1 MeV), does not separate the double-charge-transfer process from the full charge-stripping process

$$H^+ + H_2 \rightarrow H^+ + H_2{}^{2+} + 2e\ .$$

The experiment reported here clearly confirms the capability of the double-charge-transfer technique for measuring exact double-ionization energies.

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