# *DETECTION OF $HeH_2^+$ IONS AND LONG-LIVED HIGHLY EXCITED MOLECULAR AND ATOMIC STATES*

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It is shown that highly excited long-lived states of hydrogen molecules and atoms, and of helium, neon, argon, krypton, and xenon atoms are formed when electrons collide with hydrogen molecules and inert-gas atoms. Highly excited long-lived states of nitrogen, oxygen, hydrogen and carbon atoms are formed when there are collisions between electrons and nitrogen, oxygen, water, and ethylene molecules. In a mixture of helium with hydrogen, $HeH_2^+$ ions were discovered in addition to the known ions.

## 1. INTRODUCTION

COLLISIONS of electrons with atoms and molecules produce ions of various charges and particles excited to various extents. The excitation of metastable and low-energy short-lived states of atoms and molecules was investigated in [1-4].

From the quantum theory of the hydrogen atom, it is known [5] that high-energy quantum levels have long lifetimes. The average lifetime $T_n$ depends on the principal quantum number n as $T_n \propto n^{4.5}$.

Highly excited states of hydrogen atoms have been discovered in experiments on the ionization of these atoms in electric [6] and magnetic [7] fields. The excitation was retained for $\gtrsim 10^{-6}$ sec in hydrogen atoms whose principal quantum number was greater than six. It has been shown [8] that highly excited long-lived states of $He^+$ ions, which are hydrogen-like, are formed when electrons collide with helium atoms. Highly excited long-lived states of singly, doubly, and triply charged ions of other inert gases and of mercury have been discovered in experiments on the ionization of ions by means of electrons.[8,9] The generality of this effect and its independence of the electron structure of the original atoms has led to the suggestion [9] that, in these cases, the electron states of highly excited long-lived many-electron ions are hydrogen-like, i.e., in these ions, only one of the electrons is excited to a state with a large principal quantum number, and the remaining electrons are not excited.

Starting from an experimental study of highly excited ions and using published theoretical premises, it was concluded [9] that highly excited hydrogen-like states of atoms should be formed in electron-atom collisions. In 1964, Cermak and Herman [10] proved experimentally the formation of highly excited states in inert-gas atoms.

The purpose of the present work was to detect highly excited long-lived states of atoms and molecules. We were also interested in investigating the processes that occur when excited atoms and molecules collide with unexcited ones.

## 2. APPARATUS AND OPERATION METHOD

The work was carried out using a mass spectrometer of the 60° type with an ion trajectory of 200 mm radius. The ion source, shown schematically in Fig. 1, had two chambers I and II about 5 mm apart. In the first chamber, the electron beam ionized and excited the gas at a pressure of $10^{-5}$-$10^{-4}$ torr. The residual pressure was $\approx 5 \times 10^{-7}$ torr. The excited and unexcited atoms and molecules of the gases which had been admitted to the first chamber, passed to the second chamber. The electrons and ions were retained in the first chamber by electric and magnetic fields. It was evident that because of the finite lifetime of atoms and molecules in their excited states, the second chamber could receive only the

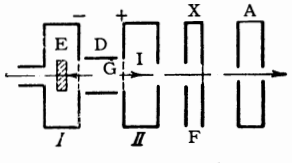


FIG. 1. Schematic representation of a two-chamber ion source: E – electrons; D – deflecting electrodes; G – grid; I – ions; X – extracting, F – focusing, and A – accelerating electrodes.

particles in metastable and highly excited states. To record the neutral particles in long-lived highly excited states, we used the second impact method, employing the following processes:

1) The ionization of atoms and molecules M when they collide with highly excited molecules and atoms A*:

$$A^* + M \rightarrow A + M^+ + e. \quad (1)$$

2) The ionization of highly excited atoms and molecules near a metal surface Me:

$$A^* + Me \rightarrow A^+ + Me. \quad (2)$$

A similar process was used in [8,11] to detect highly excited ions.

The metastable states of atoms $A^m$ were recorded during the process of their collision with the molecules M, whose ionization potentials were not greater than the excitation energy of the atoms:

$$A^m + M \rightarrow A + M^+ + e. \quad (3)$$

It will be shown below that in the processes (1) and (3), not only molecular ions of the initially present molecules are formed but also "fragment" ions, resulting from the dissociation of molecular ions.

The ion currents were measured with an ÉMU-3 electrometer amplifier and recorded automatically on the chart of an ÉPP-09 electronic potentiometer recorder. The electron energy was varied by means of a slide wire placed on the axis of the drum carrying the chart. Thus the ion current was recorded automatically as a function of the change in the electron energy. The electron energy was measured to within ±0.3 eV. The total electron emission from the cathode usually amounted to ≈ 0.5—1.0 mA. The mass spectrum was resolved by varying the magnetic field intensity. The ions were accelerated by a voltage of 2800 V.

## 3. RESULTS OF EXPERIMENTS AND DISCUSSION

a) Formation of atoms and molecules in long-lived highly excited states. The present author investigated the processes (1), (2) and (3), which took place when pure substances ($H_2$, He, Ne, Ar, Kr, Xe, CO, $H_2O$, $C_2H_4$), air, and binary mixtures of inert-gas atoms with molecular gases were admitted to the ion source. A study was made of the influence of the electron energy, the electron current, and the gas pressure on the ion yield in the three processes.

When carbon monoxide, air, water, or ethylene molecules at a pressure of $\approx 5 \times 10^{-5}$ torr were admitted to the ion source, no molecular ions were recorded if the electrometer amplifier had a sensitivity of $2 \times 10^{-14}$ A. Only the "fragment" atomic ions $N^+$, $O^+$, $H^+$, $C^+$ were found. These ions were formed by the dissociation of the original molecules, due to electron impact, into atoms in highly excited states, and the ionization of these atoms by the process (2).[1)] When electrons collided with the molecules in the first chamber of the ion source, such atoms could be formed by one of several processes. For example,

$$\begin{aligned} &C_2H_4 + e \rightarrow C_2H_3 + H^* + e, \\ &C_2H_4 + e \rightarrow C_2H_2 + H + H^* + e, \\ &C_2H_4 + e \rightarrow C_2H_3^+ + H^* + 2e \text{ etc.} \end{aligned} \quad (4)$$

The addition of helium, neon or argon to air, water or ethylene produced molecular ions $N_2^+$, $O_2^+$, $H_2O^+$ and $C_2H_4^+$. In this case, those molecular and fragment ions were formed whose appearance potentials did not exceed the excitation energy of the inert-gas atoms. The most probable process in the collisions of excited argon atoms with ethylene molecules was the formation of the molecular ions $C_2H_4^+$. These ions were formed during the collision with metastable (3) and highly excited (1) argon atoms, which can be seen from the dependences given in Fig. 2.

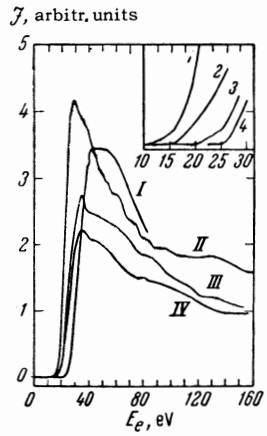


FIG. 2. Dependences of the ion current J on the electron energy $E_e$: I – $Ne^* + Me \rightarrow Ne^+$, II – $H_2^* + Me \rightarrow H_2^+$, III – $O_2 + Ne^* \rightarrow O_2^+ + Ne + e$, IV – $N_2 + Ne^* \rightarrow N_2^+ + Ne + e$. In the top right hand corner are given the initial portions of similar dependences for the processes: 1 – $C_2H_4 + Ar^* \rightarrow C_2H_4^+ + Ar + e$, 2 – $C_2H_4 + Ar^* \rightarrow C_2H_3^+ + H + Ar + e$. $C_2H_4 + Ar^* \rightarrow C_2H_2^+ + (H_2) + Ar + e$. $Ar^* + Me \rightarrow Ar^+$, 3 – $H_2O + He^* \rightarrow H_2O^+ + He + e$, 4 – $He^* + Me \rightarrow He^+$.

[1)] Moreover, highly excited atoms (particularly hydrogen atoms), formed by molecular dissociation, may have kinetic energies of the order of several electron-volts, sufficient for the ionization of these atoms in collisions with molecules.

The fragment ions $C_2H_3^+$ and $C_2H_2^+$ appeared only as a result of the collision of ethylene molecules with highly excited argon atoms (1). All this was due to the energy conditions in the inelastic process. The ionization potential of ethylene is 10.56 eV.[12] The appearance potentials of the $C_2H_3^+$ and $C_2H_2^+$ ions are, respectively, 14.0 and 13.5 eV. The energies of the metastable states of argon,[13] $^3P_0$ and $^3P_2$, are 11.66 and 11.43 eV, respectively. The energies of the highly excited states of argon are close to its ionization potential, which is 15.76 eV. In the reaction of argon with ethylene, far fewer (by a factor of 5—10) $C_2H_3^+$ and $C_2H_2^+$ ions were formed than $C_2H_4^+$ ions, since the fragment ions were produced only by one process (1), and the molecular ions were produced by the two processes (1) and (3). Obviously, considerable energy was evolved in the formation of the $C_2H_4^+$ ions in the process (1), which was sufficient to dissociate these ions provided it was used almost completely to excite the $C_2H_4^+$ ions. However, a considerable part of this excess energy could be lost as the kinetic energy of the knocked-out electron, which led to the formation of stable $C_2H_4^+$ ions.

When ethylene molecules collided with metastable and highly excited He and Ne atoms the fragment ions $C_2H_2^+$ were most likely to be formed in the former case, and the $C_2H_3^+$ ions in the latter case. In these cases, the difference between the intensities of the fragment and molecular ion beams was small (a factor of 1.5-2). From these data, we can see that when molecules are ionized by collisions with excited atoms the excess energy is frequently carried away by electrons.[2)] This is the characteristic feature of the ionization processes taking place in collisions involving excited atoms, and distinguishes the processes from those by which molecules are ionized by charge exchange on colliding with ions. This results in a large difference between the mass spectra of the same molecules ionized by these two processes. For example, in the charge exchange

$$Ar^+ + C_2H_4 \rightarrow Ar + C_2H_4^+,\ C_2H_3^+,\ C_2H_2^+, \qquad (5)$$

investigated by Cermak and Herman,[14] 25 times fewer $C_2H_4^+$ ions were formed than $C_2H_3^+$ ions, and 7 times fewer than $C_2H_2^+$ ions.

$O_2^+$, $N_2^+$ and $H_2^+$ ions are formed by the processes (1) and (3) when the corresponding molecules collide with highly excited and metastable atoms of neon and helium, and this gives rise to kinks in the curves of Fig. 2 and shifts their maxima toward low electron energies. The intensities of the currents of these ions, as well as the currents of the $C_2H_4^+$, $C_2H_3^+$, $C_2H_2^+$ ions, increase linearly as the pressure of the corresponding original gases and the pressure of the neon and helium increase.

$H_2^+$, $He^+$, $Ne^+$, $Ar^+$, $Kr^+$, and $Xe^+$ appear when pure gases and their mixtures are admitted to the ion source. The intensities of the ion currents are directly proportional to the initial gas pressure and the electron current. It is evident from the data[3)] given in Fig. 2 that these ions appear at electron energies close to the ionization potentials of the corresponding inert-gas atoms and hydrogen molecules. Consequently, these ions are formed by the process (1) from highly excited states of atoms and molecules,[4)] adjoining the continuous spectrum.

The addition of helium or neon to the hydrogen increases considerably the yield of $H_2^+$ ions, which is due to the processes (1) and (3).

The shape of the curves in Fig. 2 is characteristic. At low electron energies, there is a rapid rise up to a sharp maximum lying at an electron energy less than double the ionization energy of the corresponding inert gas atoms and $H_2$ molecules. This is followed first by a steep slope and then by regions having more gradual slopes. The curves in Fig. 2 differ considerably from the traditional curves for the ionization of atoms and molecules and are similar to the well-known [3,13] excitation functions of atoms. It is interesting to note that the corresponding dependences representing the excitation functions of highly excited states of ions [8,9] have a similar form. In our case, the curves of Fig. 2 represent the excitation functions of the metastable and highly excited states of inert gas atoms and hydrogen molecules.

During the course of the present work, a more recent paper of Cermak and Herman appeared [10], in which they showed that inert-gas atoms colliding with electrons were ionized to states with large quantum numbers. Our results on the de-

[2)] Otherwise, $C_2H_4^+$ ions should not be formed when ethylene molecules collide with excited neon and helium atoms, since the energies evolved in the processes (1) and (3) are sufficient for the dissociation of these ions.

[3)] Figure 2 gives some of the results.

[4)] Highly excited states of the hydrogen molecule are formed as a result of the excitation of only one electron by electron collisions. If the excited electron is sufficiently far from the nucleus, the state of the molecule may be regarded as hydrogen-like.[15]

tection of highly excited inert-gas atoms are in full agreement with this conclusion. There is as yet no information on the formation of highly excited stable molecular states due to electron impact. Cermak and Herman [10] noted that stable highly excited molecules of nitrogen, ethylene, carbon monoxide and n-butane were not formed by electron impact. The present author has not detected stable highly excited states of the first three of these molecules (n-butane was not investigated) or water or oxygen molecules. However, as mentioned earlier, stable highly excited hydrogen molecules were formed.

In principle, one electron may be strongly excited when electrons collide with other molecules (and not only with hydrogen molecules and inert-gas atoms). However, this is insufficient to make molecules stable in highly excited states. Molecules may dissociate if the electron transition produces a repulsive state or a stable electron state above the dissociation threshold. Highly excited molecular states may, moreover, undergo auto-ionization and thus leave the molecular beam entering the second chamber of the ion source.

Consequently, the lifetimes of excited molecular states are governed not only by the degree of excitation of one of the electrons but also by the type of the state and its position relative to the Franck-Condon region, and the auto-ionization lifetime. If, owing to electron transitions that transfer molecules to highly excited states, most of the molecules leave in some way the molecular beam entering the second chamber, the remaining small fraction of highly excited molecules may not be detected because of the limited sensitivity of the recording apparatus.

We have remarked earlier that molecular ions of ethylene, water, carbon monoxide, nitrogen, and oxygen were not observed. Only the fragment atomic ions were obtained. However, at a higher pressure ($\approx 10^{-4}$ torr) and a higher sensitivity ($\approx 2 \times 10^{-15}$ A) and electron current ($\approx 5$ mA), it was possible to record the currents of the molecular and fragment ions of these substances. These results will be considered separately. We note here only that the molecular ions of ethylene are formed by the collision of highly excited hydrogen atoms with ethylene molecules:

$$H^* + C_2H_4 \rightarrow H + C_2H_4^+ + e. \quad (6)$$

Highly excited hydrogen atoms taking part in this reaction are obtained as a result of electron collisions with ethylene molecules in the processes given by Eq. (4).

b) Formation of $HeH_2^+$, $HeH^+$ and other ions in a mixture of hydrogen and helium. The ions $HeH^+$, $H_3^+$, $He_2^+$, $H_2^+$, $He^+$, $H^+$ are formed by electron impact in a mixture of helium and hydrogen. It has been shown [16,17] that $HeH^+$ ions are formed by ion-molecule reactions when vibrationally excited $H_2^+$ ions collide with helium atoms:

$$H_2^+ + He \rightarrow HeH^+ + H. \quad (7)$$

$H_3^+$ ions are formed [17] in the process:

$$H_2^+ + H_2 \rightarrow H_3^+ + H. \quad (8)$$

The cross section for the above process has been calculated.[18] $He_2^+$ ions are formed [19,20] in the collision of excited and unexcited helium atoms:

$$He^* + He \rightarrow He_2^+ + e. \quad (9)$$

The other ions are formed by electron collisions with helium atoms and hydrogen molecules. $HeH_2^+$ ions have not yet been observed.

In a study of the mass spectrum of a mixture of helium and hydrogen, formed in the second chamber of the ion source, the present author de-

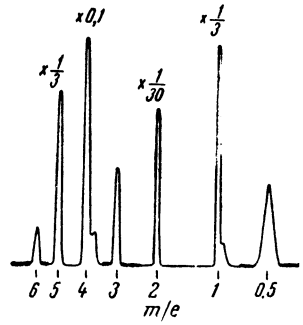


FIG. 3. Mass spectrum of a mixture of helium with hydrogen, formed in the second chamber of the ion source. The scale coefficients are given above each peak. The electron energy was 50 eV, the helium pressure $8 \times 10^{-5}$ torr, and the hydrogen pressure $7 \times 10^{-5}$ torr.

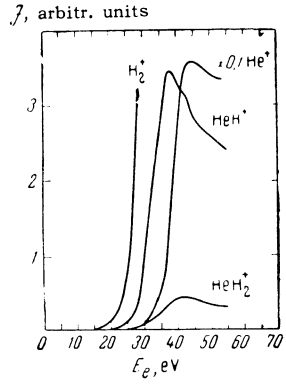


FIG. 4. Influence of the energy of the electrons, which excite the gas in the first chamber, on the intensity J of the ions leaving the second chamber of the ion source. The intensity of the $He^+$ ions is scaled down in the figure by a factor of 10.

tected, apart from the ions mentioned above, a peak corresponding to m/e = 6 (m is the mass and e is the charge of ions). A study showed that this peak was formed by $HeH_2^+$ ions appearing in the process

$$He^* + H_2 \rightarrow HeH_2^+ + e. \quad (10)$$

Figure 3 shows the mass spectrum of a mixture of helium and hydrogen, while Figure 4 gives the dependence of the ion currents on the electron energy. The broad peak at m/e = 0.5 is due to protons appearing as a result of single collisions of $H_2^+$ ions with helium atoms and hydrogen molecules in the space between the ion source and the analyzing magnetic field. The amplitude of this peak varies as $p^2$, where p is the gas pressure in the analyzer space. The peak at m/e = 1 is due to protons appearing as a result of the ionization of highly excited hydrogen atoms near the metal surface of the grid in the process (2), as well as by the collision of metastable and highly excited helium atoms with hydrogen molecules in the processes (3) and (1). The peak at m/e = 2 is formed by $H_2^+$ ions that appear as a result of the collisions of $H_2$ molecules with helium atoms in the processes (1) and (3) (this is indicated by kinks in the curve near 21 and 25 eV), and as a result of the ionization of highly excited hydrogen molecules in the process (2). Under the conditions used to obtain the mass spectrum shown in Fig. 3, the latter process was less likely than the former.

The amplitudes of the peaks at m/e = 1 and m/e = 2 depend linearly both on the hydrogen and on the helium pressure. The peak at m/e = 3 is formed by $H_3^+$ ions. The present author did not investigate in detail the mechanism of the formation of these ions in a mixture of helium and hydrogen. However, one process of $H_3^+$ ion formation was established. The similar values of the appearance potentials of $H_3^+$ ions and highly excited $H_2^*$ molecules and the quadratic dependence of their intensity on the hydrogen pressure indicated a formation process of the type

$$H_2^* + H_2 \rightarrow H_3^+ + H + e. \quad (11)$$

The ratio of the intensity of the $H_3^+$ ions to that of the $H_2^+$ ions decreased rapidly on the addition of helium to hydrogen if the electron energy $E_e$ was greater than 20 eV but it was not affected at $E_e$ < 20 eV. The formation of $H_3^+$ ions in the process

$$H^* + H_2 \rightarrow H_3^+ + e \quad (12)$$

was insignificant under these experimental conditions.

This conclusion followed from experiments on a mixture of hydrogen and ethylene. For example, the addition of ethylene to hydrogen did not raise the intensity of the $H_3^+$ ions, although the intensity of the $H^+$ ions increased considerably. The absence of a large contribution from the process (12) to the intensity of the $H_3^+$ ions was obviously due to the relatively high kinetic energy of the highly excited hydrogen atoms.

The peak at m/e = 4 is due to $He^+$ ions, appearing as a result of the ionization of highly excited helium atoms in the process (2). The peak at m/e = 5 is due to $HeH^+$ ions which appear as a result of the process

$$He^m + H_2 \rightarrow HeH^+ + H + e. \quad (13)$$

As indicated by the dependences in Fig. 4, the $HeH^+$ ions appear at an energy close to the excitation potentials of metastable helium atoms [21] in the states $1s2s^3S_1$ (19.8 eV) and $1s2s^1S_0$ (20.6 eV). From the dependences in Fig. 4, it is impossible to establish which of these two states is, or whether both of them are, responsible for the formation of $HeH^+$ ions. At higher electron energies, the $HeH^+$ ions also begin to form as a result of the collisions of highly excited helium atoms and hydrogen molecules, according to the reaction

$$He^* + H_2 \rightarrow HeH^+ + H + e.. \quad (14)$$

The current of $HeH_2^+$ ions became noticeable at an electron energy of about 25 eV, which indicated the participation of highly excited long-lived helium atoms in the process (10). The slight intensity of the $HeH_2^+$ ions made it impossible to establish the formation of these ions when metastable helium atoms collided with hydrogen molecules. The amplitudes of the peaks at m/e = 5 and m/e = 6 rise linearly both with increase of the hydrogen pressure at a constant helium pressure, and with increase of the helium pressure at a constant hydrogen pressure. This is shown in the table, which gives also the ratio

Influence of the helium pressure on the ratio of the current of $HeH^+$ and $HeH_2^+$ ions on the current of $He^+$ ions. The electron energy was 50 eV, and the hydrogen pressure $7 \times 10^{-5}$ torr

| Helium pressure, $10^{-5}$ torr | Ratio of currents | | | Helium pressure, $10^{-5}$ torr | Ratio of currents | | |
|---|---|---|---|---|---|---|---|
| | $HeH^+/He^+$ | $HeH_2^+/He^+$ | $HeH^+/HeH_2^+$ | | $HeH^+/He^+$ | $HeH_2^+/He^+$ | $HeH^+/HeH_2^+$ |
| 1.7 | 1.0 | 1.0 | 13.3 | 5.0 | 0.90 | 0.87 | 13.8 |
| 3.0 | 0.95 | 0.95 | 13.6 | 6.0 | 1.0 | 1.0 | 13.3 |
| 4.0 | 1.0 | 0.95 | 14.3 | 8.0 | 1.1 | 1.0 | 14.0 |

of the intensities of the $HeH^+$ and $HeH_2^+$ ions at various helium pressures. The value of this ratio is constant within the experimental error ($\approx 15\%$). It is evident from these data, moreover, that, under the conditions considered, the role of ion-molecule reactions in the second chamber of the ion source is small. The peak at m/e = 8 corresponding to the $He_2^+$ ions, is not given in Fig. 3. Under the present experimental conditions, the intensity of $He_2^+$ ions was very small.

Thus the results given indicate definitely the formation of $HeH_2^+$ ions in the collision of highly excited helium atoms with hydrogen molecules. $HeH^+$ and $H_3^+$ ions are formed when excited helium atoms and $H_2$ molecules collide with hydrogen molecules. The present results do not mean the rejection of the processes (7) and (8) in the formation of $HeH^+$ and $H_3^+$ ions, but they supplement these processes since they indicate new ways of forming these ions. In [16,20], the processes of the formation of $HeH^+$ and $H_3^+$ ions were identified by measuring the appearance potentials of these ions and comparing them with the appearance potentials of other ions, formed in a mixture of helium and hydrogen. Obviously, this method makes it difficult to distinguish processes in which ions and highly excited particles participate, since they appear at similar electron energies. The present results force us to assume that some fraction of $HeH^+$ and $H_3^+$ ions was formed, under the conditions used in [16,20], in the reactions (11), (13), and (14) involving neutral particles, and not only as a result of ion—molecule reactions, which were the only ones considered in [16,20].

At present, there are still no quantitative data on the role of the processes in which excited particles participate, as compared with ion-molecule reactions. Qualitative ideas based on the large dimensions of highly excited particles and the role played by energy resonances in such processes force us to assume that the role of excited particles in the formation of "unusual" ions is quite important.

It has been mentioned that $HeH^+$ ions form [16] as a result of the ion-molecule reaction (7). It would seem that with the method used here (a two-chamber ion source) one could attempt to establish the process of the formation of $HeH^+$ ions as a result of the collisions between highly excited hydrogen molecules and helium atoms, i.e.,

$$H_2^* + He \rightarrow HeH^+ + H + e. \qquad (15)$$

However, the present author was unable to establish such a process. The explanation for this may be as follows. From energy considerations, it follows that the reaction (15), like (7), is endothermic if hydrogen molecules or ions are in the ground vibrational state. Koch and Friedman[16] have shown that the process (7) involves $H_2^+$ ions, excited above the fourth vibrational level. Consequently, the endothermic nature of the reaction (15) may be overcome by the vibrational excitation of hydrogen molecules. However, highly excited hydrogen molecules may auto-ionize rapidly [22] so that they leave the molecular beam entering the second chamber of the ion source. Another reason may be the insufficient sensitivity of the recording apparatus.

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