Reaction of carbon dication C²⁺ with O₂, N₂, CO, and HD at low temperatures: Experimental study using a 22-pole ion trap

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We present experimental studies of reactions of doubly charged carbon cation (carbon dication, C^{2+} , C III) with O_2 , N_2 , CO, and HD molecules. A temperature-variable cryogenic linear 22-pole radio frequency ion trap was employed to obtain reaction rate coefficients and their temperature dependencies in the range from 40 to 300 K. The measured coefficients are almost independent of the temperature at the covered range. At 60 K the reaction rate coefficients are $1.4(3) \times 10^{-9}$ cm³ s⁻¹ for O_2 , $1.9(4) \times 10^{-12}$ cm³ s⁻¹ for N_2 , $8(2) \times 10^{-12}$ cm³ s⁻¹ for CO, and $1.5(5) \times 10^{-10}$ cm³ s⁻¹ for HD.

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I. INTRODUCTION

Reactions of doubly charged carbon cation have been a topic of interest in many research areas such as astrophysics, plasma chemistry, and high-temperature plasma [1–3]. The reactions of C^{2+} with molecules are important for fundamental theoretical physics because they greatly differ from reactions of singly charged ions in dynamics. A general description of bimolecular reactions of dications, their mechanism, dynamics, and kinetics was given in recent reviews by Price *et al.* [4] and by Herman [5].

From an astrophysical perspective, reactions of C^{2+} with molecules are relevant in regions where the dications are produced in abundance—in the interstellar matter exposed to x-ray radiation, for example. There, CH^+ ions were assumed to be produced in reactions of C^{2+} ions with dihydrogen molecules [6,7]. The C^{2+} ions have been detected in the Galilean moon Io's ionosphere [8], but their role in the planetary atmospheric chemistry has not yet been elucidated.

Reactions of dications at 300 K and slightly above were studied experimentally in an ion trap by Gao and Kwong [9] and in SIFT apparatuses [10,11]. To understand the reactivity of C²⁺ ions in a dilute dihydrogen gas at temperatures relevant to astrochemistry (from 300 K down to 15 K), a cryogenic ion trap was employed recently by Plašil *et al.* [12]. The rate coefficient of the C²⁺ + H₂ reaction turned out to be nearly constant in the temperature range covered, $k_{H_2}(100 \text{ K}) = 1.5(2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, with a value that is 4– 5% of the corresponding Langevin collisional rate coefficient. The dominant product appeared to be the C⁺ ion and only a minor production of CH⁺ ions was observed.

Despite its importance for astrochemistry, plasma physics, and fundamental theoretical physics, not too many experimental studies have been carried out on the topic of reactions between C^{2+} and neutral molecules.

Here we present results we obtained in experimental studies of reactions of C^{2+} dications with O_2 , N_2 , CO, and

HD molecules at temperatures from 40 to 300 K. Reported are temperature dependencies of the reaction rate coefficients. In the text, the reaction-rate coefficients are distinguished by the lower index, which indicates the reactant molecule. The new results are compared with data from previous experiments if available.

II. EXPERIMENTAL

To study the reactions of C^{2+} dication with diatomic molecules O₂, N₂, CO, and HD, we used a temperaturevariable cryogenic linear 22-pole radio frequency ion trap (22PT) that confines ions produced out of the confinement volume in a so-called storage ion source. The apparatus and its operation principles have already been described in earlier works [12–16], so only a very short description will be given here with an emphasis on some specific aspects of the present study.

A. Production of carbon dication

Dications C^{2+} are produced in the storage ion source by the electron bombardment of a C_2H_4 gas. From there, they are periodically extracted into a quadrupole mass filter and then diverted by a quadrupole bender into the ion trap (for a detailed description, see Refs. [12,15]). The kinetic energy of C^{2+} ions entering the trap is typically not higher than 0.1 eV. Considering the radiative deexcitations of C^{2+} [17], it is obvious that more than 99.9% of all C^{2+} ions are in the four lowest internal states at the time of the injection to the trap. In our previous work [12], we discussed the deexcitation of the three excited states of C^{2+} (${}^{3}P_{0}^{0}$, ${}^{3}P_{1}^{0}$, and ${}^{3}P_{2}^{0}$) in collisions with helium. We concluded that it is very likely we measure the reaction with C^{2+} in the ground-state ${}^{1}S_{0}$.

B. 22-PT cryogenic ion trap

The ion-trapping technique implemented in our apparatus was developed by Gerlich and Horning [18]. In this design, 22 rods (with a diameter of 1 mm) are arranged into the shape of a cylinder. An ion-trapping, ponderomotive potential

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is formed along the trap axis in the radial direction by applying radio-frequency electric potentials with opposite phases to neighboring rods. In the axial direction, the ion confinement is secured by a static potential barrier formed by hollow cylindrical electrodes. Applying a suitable potential to these electrodes, the trap can be set open to ions coming from the ion source or set to release the contents toward an ion detection system (basically a quadrupole mass spectrometer).

The body of the 22-pole ion trap is placed in a copper box that is attached to a cold head of a closed-cycle helium refrigerator. The temperature of the copper box can be varied from 300 to 10 K. The temperature on the body of the ion trap (T_{22PT}) is directly measured with silicon diodes.

The ion source, the ion trap, the detection system, the ion optics, and the cold head are placed in a UHV vacuum chamber. During the measurements, a small amount of helium gas (with a number density of 10^{13} to 10^{14} cm⁻³) is let into the confinement region to cool the ions in collisions. For the reaction studies, a small amount of the reactant gas (variable in a range from 10^{10} to 10^{12} cm⁻³) is mixed into the helium buffer gas. The number density of molecules was monitored by the spinning rotor gauge at room temperature connected directly to the trap volume—the values were corrected for thermal transpiration.

C. Thermalization and reaction of carbon dication

In the standard measuring procedure, a nearly constant number of primary C^{2+} dications is injected periodically into the trap and allowed to react with reactant gas molecules for a chosen period. On injection, the dications undergo the process of thermalization in which they lose the initial 0.1 eV kinetic energy in hundreds of collisions (on average) with buffer gas molecules before meeting a reactant molecule of interest. This equilibration justifies an assumption that ions can be characterized by the Maxwell-Boltzmann velocity distribution parameterized by the kinetic temperature. A difference between this and the temperature of the trap is usually caused by the so-called radio-frequency heating. This happens during an energy exchange between the ion and the oscillatory electric field that takes place at turning points of ion trajectories in the vicinity of trap rods.

In several recent experimental studies, the kinetic temperature of ions stored in a trap was characterized by measuring the Doppler broadening of absorption lines of the ions [19,20]. The measurements have shown that the collisional temperature (here denoted as *T*) does not exceed T_{22PT} by more than 10 K. In the present text we define the collisional temperature as $T = T_{22PT} + 5$ K with an uncertainty of ± 5 K (for further details and discussion, see Refs. [15,21–24]). The validity of this approximation was also verified by measuring temperature dependencies of reaction-rate coefficients of several endothermic ion-molecule reactions (e.g., Refs. [15,25]).

D. Data analysis

The reactions of stored ions with reactant gas molecules change the ion composition in the ion trap. To analyze the kinetics of the ion-molecule reactions, reactant and product ions are released from the trap, mass analyzed, and counted



FIG. 1. Reaction of C²⁺ dication with O₂: Time evolutions of the numbers of ions as measured after the injection of C²⁺ into the trap. The sum of charges (Σ) is indicated by the stars. The dotted line shows the fit of the monoexponential decrease to numbers of C²⁺ ions with characteristic time τ . The dashed line shows the decrease of $N_{C^{2+}}$ without the reactant gas. The production of O₂⁺ and CO⁺ was also observed in the experiment but the relative populations of these ions are below 0.5% of the initial number of the primary C²⁺ ions.

using a quadrupole mass spectrometer equipped with a microchannel plate detector. To judge how a proportionality between the number of ions stored and the number detected is maintained across a wide mass range, we calibrate the mass spectrometer by measuring the rate coefficients of well-known ion-molecule reactions. Based also on these measurements, we can safely assume that the numbers of ions in the ion trap and of those that make it to the detector are proportionally linked. This allows us to use a simple relation to evaluate the rate coefficients of reactions of C²⁺ ions from a change of ion number measured over a specific period.

In principle, detailed monitoring of the chemical composition of the ion cloud measured at multiple confinement time steps (over many repetitions of the experiment) enables us to evaluate branching ratios of the reactions as well. However, in the case of C^{2+} -molecule chemical reactions, quite a few product ions escape the trapping volume immediately on the reaction event because they gain high kinetic energysee Refs. [4,5,26] for reviews on the dynamics of chemical reactions of multiply charged cations. Therefore, we will determine the reaction-rate coefficients and their temperature dependencies, not branching ratios, here. We will illustrate our data analysis procedure with an example of the $C^{2+} + O_2$ reaction. Figure 1 represents a typical ion composition evolution measured in our trap. A decline of C^{2+} number in time to which we further refer as $N_{C^{2+}}(t)$ following the rule of putting corresponding chemical species in subscripts- along with $N_X(t)$ for several other species X is drawn. The plotted data were obtained at temperature T = 85 K, helium number density [He] = 1.3×10^{14} cm⁻³, and oxygen number density $[O_2] = 9.5 \times 10^{10} \text{ cm}^{-3}$. Among the ions detected (C²⁺, O⁺, C^+ , O_2^+ , and CO^+), the dominant product ions were measured to be \overline{O}^+ and \overline{C}^+ . Ions with relative populations below 0.5% of the initial number of primary C^{2+} are not included in the figure. This is partly because it is difficult to distinguish between primary and secondary products on this timescale



FIG. 2. The dependence of the time evolutions of the number $N_{C^{2+}}(t)$ of the C²⁺ ions on the number densities of O₂. The plotted data were measured at T = 86 K and [He] = 1.3×10^{14} cm⁻³. The lines represent the exponential fits of the individual data sets. The nearly horizontal dashed line represents the time evolution of the number of C²⁺ ions in the absence of the O₂ reactant gas—normalized to 100 ions. The dependence of the obtained reaction-rate r_{O_2} versus [O₂] is shown in the inset.

and because the corresponding signal is already at the level of noise.

Also plotted is the sum of charges carried by the ions (two charges on C^{2+} are considered). The time evolution of the sum indicates that the number of charges in the trap is not constant and decreases during the reaction of C^{2+} dications. The decrease is caused by the escape of the product ions (as mentioned above). The decrease of $N_{C^+}(t)$ indicates that the C^+ ions further react with O₂ [27].

A rough estimate is that nearly 90% of the ions produced in the reaction of C^{2+} with O_2 escape from the trap, making it impossible to evaluate the individual reaction branches quantitatively from the product yields. Consequently, we only assessed the overall reaction-rate coefficient from $N_{C^{2+}}(t)$.

The dashed line in Fig. 1 indicates a normalized $N_{C^{2+}}(t)$ decay line measured with no O₂ reactant gas present in the trap (while all the other parameters were kept the same). The decay time constant obtained is larger than 15 s and quantifies the influence of reactions with a background gas from the vacuum system. We observe that the value depends on the temperature of the trap. Note that the characteristic C^{2+} reaction time, measured in the experiments with the reactant gas, is many times shorter (for the data in Fig. 1 it is below 10 ms). The monoexponential nature of the C^{2+} decays observed throughout a range of O₂ number densities, illustrated in Fig. 2, allows for a straightforward evaluation of the $C^{2+} + O_2$ reaction-rate coefficients k_{O_2} as demonstrated by a dependence of the reaction-rate r_{O_2} on $[O_2]$ in the inset of the figure. To compare the decays measured with and without the reactant gas, the time evolution measured without the reactant gas is also included in Fig. 2.

To investigate whether ternary He-assisted reactions take place, the dependence of k_{O_2} on the He number density was measured at several temperatures. We did not observe any dependence of k_{O_2} on [He] in a range from 3×10^{11} to 3×10^{14} cm⁻³. Similar measurements were also made for





FIG. 3. Dependencies of the reaction-rate $r_{\rm CO}$ of the reaction of C²⁺ dications with CO on the number density of CO. The data were measured at T = 59 K and T = 72 K with [He] = 1.54×10^{14} cm⁻³ and [He] = 1.44×10^{14} cm⁻³, respectively. The corresponding values of the binary reaction-rate coefficients $k_{\rm CO}$ are given by the slopes of the obtained dependencies.

reactions of C^{2+} with the other three reactants; the results were the same—no observed dependence on [He].

We also measured the dependencies of the reaction rates (r_X) on the number density of a reactant gas [X]. Figure 3 represents two such measurements carried out with CO as the reactant at temperatures of 59 and 72 K. The linearity of the dependences reveals that the reaction of C²⁺ ions with CO is predominantly of a binary nature. The temperature dependencies of the rate coefficients of all four studied reactions were measured for temperatures from 40 up to 300 K. As an example, the raw data obtained for the rate coefficient of the C²⁺ + O₂ reaction are plotted in Fig. 4. We can see that the



FIG. 4. Temperature dependence of the measured $C^{2+} + O_2$ reaction-rate coefficient k_{O_2} . Small circles indicate values of the reaction-rate coefficient k_{O_2} obtained from the time evolutions of the number of C^{2+} ions due to their reaction with O_2 in the ion trap. The large rhomboids indicate the binned values of k_{O_2} . Here the vertical error bars indicate a statistical error that originates from the binning uncertainty propagating from the temperature uncertainty of ± 5 K. In addition, there is a 20% systematic uncertainty in the values due to the inaccuracy of the reactant pressure measurement.



FIG. 5. Temperature dependencies of the rate coefficients of the reactions of C^{2+} dications with O_2 , N_2 , CO, and HD molecules (molecules of the reactant are indicated next to symbols). The vertical error bar here includes the 20% systematic uncertainty in the reactant pressure measurement as an independent effect. The plotted temperature dependence of the rate coefficient k_{H_2} (indicated by crosses) for the reaction of C^{2+} with H_2 is adopted from our previous study [12]. The thermal values of the rate coefficients of the reactions with O_2 , N_2 , and H_2 obtained in previous SIFT experiments [10] are plotted as an open rhomboid, an open triangle, and an open star, respectively. The thermal value of the rate coefficient k_{H_2} of the reaction with H_2 measured in a SIFT experiment [11] is plotted by a full square.

reaction-rate coefficient is nearly constant in the temperature range covered.

III. RESULTS AND DISCUSSION

In Fig. 5, we summarize the results we have obtained from measurements of reactions of C^{2+} with O_2 , N_2 , CO, and HD molecules. We can see that the values of the reaction-rate coefficients are very different.

A simple qualitative explanation of the electron transfer reactions between neutral and dication is possible using the Landau-Zener model [4,5]. This considers the relatively flat polarization attraction potential and the repulsive Coulomb potential of the products. If the curve crossing lies at a large interspecies separation, the coupling between the two potentials will be small and the electron transfer inefficient. On the other hand, too small of a separation leads to a very effective electron transfer at each pass. As a result, the probability of final electron transfer after two passes is small.

The electron transfer is effective in the reaction window, which is defined by the exothermicity (ΔE) of the reaction. The typical reaction window for dications lies between 2 and 6 eV [4]. The favorable exothermicities of the individual reaction channels in this range are written in bold in Eqs. (1)–(4).

In the case of molecular targets, a reaction may be more probable at low collision energies with a longer interaction time between dication and neutral. In addition, a smaller amount of translational energy needs to be distributed among the degrees of freedom of the products. However, more accurate theoretical treatments of these collisions are complicated due to the vibrational and rotational structures of the molecules.

The reaction of C²⁺ with O₂ is fast with a nearly constant reaction-rate coefficient, the value of which is close to the corresponding Langevin collisional rate coefficient $k_{\text{L-O}_2} = 2.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

$$C^{2+} + O_2 \rightarrow \begin{cases} C^+ + O_2^+ & \Delta E = 12.3 \text{ eV} \\ C^+ + O^+ + O & \Delta E = 5.6 \text{ eV} \\ C + O^+ + O^+ & \Delta E = 3.2 \text{ eV}. \end{cases}$$
(1)

There are two channels of the reaction (1) in the favorable energy window. We assume it is the reason for the high reactivity of carbon dication with molecular oxygen. The values of reaction-rate coefficients measured at 100 and 300 K are $k_{O_2}(100 \text{ K}) = 1.5(3) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ and $k_{O_2}(300 \text{ K}) = 1.6(3) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, respectively. For comparison with previous studies, we also included the value of k_{O_2} measured in the SIFT experiment at 300 K by Viggiano *et al.* [10] in Fig. 5. The agreement with the present results is very good.

The reaction of C²⁺ with N₂ (2) is very slow compared with the Langevin collisional rate coefficient $k_{L-N_2} = 2.1 \times 10^{-9}$ cm³ s⁻¹. This may be due to the lack of direct favorable reaction channels with exothermicity in the suitable energetic window and inefficient energy dissipation into the N₂⁺ vibrational states.

$$C^{2+} + N_2 \rightarrow \begin{cases} C^+ + N_2^+ & \Delta E = 8.8 \text{ eV} \\ C^+ + N^+ + N & \Delta E = 0.1 \text{ eV} \\ C + N^+ + N^+ & \text{endothermic.} \end{cases}$$
(2)

The reaction-rate coefficients at 100 and 300 K are $k_{\rm N_2}(100 \text{ K}) = 1.4(3) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ and $k_{\rm N_2}(300 \text{ K}) =$ $3.3(8) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, respectively. The measured temperature dependence of the reaction-rate coefficient has a minimum at $T \approx 160$ K. At temperatures above this minimum, the rate coefficient k_{N_2} increases with an increasing temperature toward 300 K. At 300 K, we can compare the present value with the value obtained in the SIFT experiment by Viggiano *et al.* [10]—the agreement between both results is very good. The reaction of C^{2+} with N₂ was experimentally studied also by Gao and Kwong [9] using a cylindrical radio frequency ion trap. At a temperature of 1.17×10^4 K, they obtained reaction-rate coefficient $k_{N_2} = 1.08(7) \times 10^{-10}$ cm³ s⁻¹. Their value is nearly two orders of magnitude higher than the values measured at low temperatures in the present study and the study of Viggiano et al. [10]. This can indicate a very steep temperature dependence of k_{N_2} at temperatures above 300 K. That happens to be in accordance with a theoretical model of Bacchus-Montabonel and Tergiman [28] for temperatures 400-50,000 K, which seems to predict the value of Gao and Kwong well. However, the value calculated for 400 K, $k_{\rm N_2} = 2.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, is lower than what had been measured by Viggiano et al. [10].

The collisional rate coefficient for a reaction with a molecule with a permanent dipole is higher than the Langevin's estimate and depends on temperature. The theoretical value for the reaction (3) changes slightly with temperature from 2.6×10^{-9} cm³ s⁻¹ at 60 K to 2.4×10^{-9} cm³ s⁻¹ at 150 K [29]. The experimental values are more than two orders of magnitude lower as only one channel of reaction (3) is at the bottom margin of the suitable energetic window.

$$C^{2+} + CO \rightarrow \begin{cases} C^{+} + CO^{+} & \Delta E = 10.4 \text{ eV} \\ C^{+} + C^{+} + O & \Delta E = 2.0 \text{ eV} \\ C^{+} + O^{+} + C & \text{endothermic.} \end{cases}$$
(3)

The rate coefficient $k_{\rm CO}$ of the reaction (3) was measured to be nearly constant, $k_{\rm CO}(100 \text{ K}) = 7(2) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, in the temperature range of 60–150 K. To our knowledge, this reaction was not studied previously at low temperatures. Gao and Kwong [9] mentioned above obtained the reaction-rate coefficient $k_{\rm CO} = 4.6(3) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at the temperature of $1.17 \times 10^4 \text{ K}$, which is, again, in good agreement with the model [28] that predicts a steep rise with increasing temperature. However, the value calculated for 400 K, $k_{\rm CO}(400 \text{ K}) =$ $6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, is more than one order of magnitude lower than the value measured in this study for temperatures below 150 K.

The rate coefficient of the reaction of C^{2+} with HD is nearly constant for temperatures below 200 K, $k_{\text{HD}}(100 \text{ K}) =$ $1.6(3) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, as it was observed in the case of $C^{2+} + H_2$ reaction in experiments carried out by Plašil *et al.* [12] (also plotted in Fig. 5).

$$C^{2+} + HD \rightarrow \begin{cases} C^{+} + HD^{+} & \Delta E = 8.9 \text{ eV} \\ C^{+} + H^{+} + D & \Delta E = 6.3 \text{ eV} \\ C + H^{+} + D^{+} & \Delta E = 3.9 \text{ eV} \\ CH^{+} + D^{+} & \Delta E = 10.4 \text{ eV}. \end{cases}$$
(4)

Since the permanent dipole of HD is very small, the theoretical collisional rate coefficient for the reaction (4) is close to Langevin's estimate 2.7×10^{-9} cm³ s⁻¹ at the covered temperature range.

Unlike in the reaction involving H_2 , the value of the rate coefficient with HD starts increasing at 200 K, reaching the value $k_{\rm HD}(300 \text{ K}) = 6(2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 300 K. The difference between the reactions with HD and H₂ is surprising. Petralia et al. [30] observed a similar strong inverse isotope effect in the charge transfer reaction of xenon cations with an ammonia molecule or its deuterated isotopologue. To explain this result, they proposed that during the ion-molecule reaction, kinetic energy can be dissipated into the vibrational modes of the resulting complex, a process called intramolecular vibrational redistribution (IVR). Since the rate of IVR in such a complex depends on the density of vibrational states [31], deuteration can lead to lower vibrational frequencies and thus faster IVR due to a higher density of vibrational states at given energy [32]. This would result in a longer lifetime of the deuterated complex. Since a larger lifetime and more states are involved in the energy dissipation of the deuterated complex, the deuterated complex may react faster than the nondeuterated one. We speculate that the observed temperature dependence may be due to the difference in the occupation of the lowest rotational states of H_2 and HD.

 C^+ has been observed to be the dominant product ion species in the reaction (4), but we cannot present a value for the branching ratio due to the escape of energetic product ions from the trap mentioned in the previous section. Experiments with HD were performed at temperatures as low as 15 K, but a secondary production of D_3^+ ions—which happens to have the same mass to charge ratio as C^{2+} —becomes prominent at low temperatures. That is why we can give k_{HD} just for temperatures above 45 K. For the same reason, we have not measured the rate coefficient for the $C^{2+} + D_2$ reaction.

IV. CONCLUSION AND OUTLOOK

We used a temperature variable 22-pole radio frequency ion trap to perform a series of experiments showing how the gas-phase reactions of C^{2+} dication with chosen diatomic neutral molecules (O₂, N₂, CO, and HD) are influenced by changes in variables such as a temperature or a reactant number density. The data, predominantly rates and rate coefficients for O₂, N₂, and HD molecules, were obtained for temperatures from 40 to 300 K. The rate coefficient of reaction with CO was measured in a smaller temperature range (60–150 K) to avoid an effect of condensation of CO on the walls of the trap.

The reaction-rate coefficients were evaluated from C^{2+} number decays and the number densities of neutral reactants. The evaluation from product yields was not possible because a part of the charged products escapes the trap as they gain high kinetic energy in the reactive collision. That also prevented us from identifying product branching ratios.

The rate coefficient for the reaction with O₂ has a nearly constant value $k_{O_2} \approx 1.5(3) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ in the temperature range covered in our experiments. That is approximately two-thirds of the value of the corresponding Langevin collisional rate coefficient $k_{\text{L-O}_2} = 2.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

The rate coefficient of the reaction of C²⁺ dications with HD also appeared to be nearly constant $k_{\rm HD} \approx 1.7(4) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for T < 200 K. At these temperatures, it is very close to the value for the reaction with H₂, $k_{\rm H_2} = 1.5(2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ recently measured by Plašil *et al.* [12]. However, at temperatures above 200 K $k_{\rm HD}$ increases and becomes two to three times higher than $k_{\rm H_2}$ at 300 K.

The rate coefficient $k_{\rm CO}$ of the reaction with CO was measured to be nearly constant $k_{\rm CO} \approx 7(3) \times 10^{-12}$ cm³ s⁻¹ in the temperature range covered, 200 times lower than the value of the rate coefficient for reaction with O₂.

Even smaller is the value of the rate coefficient of the reaction with N₂. The measured temperature dependence has a rather broad minimum at $T \approx 160$ K with value $k_{N_2} = 1.1(3) \times 10^{-12}$ cm³ s⁻¹. The rate coefficient is about 2000 times lower than the corresponding Langevin collisional rate coefficient $k_{L_rN_2} = 2.4 \times 10^{-9}$ cm³ s⁻¹.

We hope that the presented experimental results will encourage further theoretical research. Experimental studies of reactions of C^{2+} with other diatomic and polyatomic molecules important for astrochemistry are in preparation.

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- M. S. Povich, Doubly ionized carbon observed in the plasma tail of comet Kudo-Fujikawa, Science 302, 1949 (2003).
- [2] E. Zicler, M.-C. Bacchus-Montabonel, F. Pauzat, P. Chaquin, and Y. Ellinger, Communication: The formation of CHe²⁺ by radiative association, J. Chem. Phys. **144**, 111103 (2016).
- [3] N. Yoneda, T. Shikama, K. Hanada, S. Mori, T. Onchi, K. Kuroda, M. Hasuo, A. Ejiri, K. Matsuzaki, Y. Osawa *et al.*, Toroidal flow measurements of impurity ions in QUEST ECH plasmas using multiple viewing chords emission spectroscopy, Nucl. Mater. Energy 26, 100905 (2021).
- [4] S. D. Price, J. D. Fletcher, F. E. Gossan, and M. A. Parkes, Bimolecular reactions of the dications and trications of atoms and small molecules in the gas-phase, Int. Rev. Phys. Chem. 36, 145 (2017).
- [5] Z. Herman, Dynamics of chemical reactions of multiplycharged cations: Information from beam scattering experiments, Int. J. Mass Spectrom. 378, 113 (2015).
- [6] W. D. Langer, The formation of molecules in interstellar clouds from singly and multiply ionized atoms, Astrophys. J. 225, 860 (1978).
- [7] B. Godard and J. Cernicharo, A complete model of CH⁺ rotational excitation including radiative and chemical pumping processes, Astron. Astrophys. 550, A8 (2013).
- [8] P. D. Feldman, D. F. Strobel, H. W. Moos, and H. A. Weaver, The far-ultraviolet spectrum of the Io plasma torus, Astrophys. J. 601, 583 (2004).
- [9] H. Gao and V. H. S. Kwong, Charge transfer between C²⁺ and H₂, N₂, He, and CO at electron-volt energies, Phys. Rev. A 68, 052704 (2003).
- [10] A. A. Viggiano, F. Howorka, J. H. Futrell, J. A. Davidson, I. Dotan, D. L. Albritton, and F. C. Fehsenfeld, Reactions of Kr²⁺, Xe²⁺, and C²⁺ with atoms and molecules at 300 K, J. Chem. Phys. **71**, 2734 (1979).
- [11] D. Smith and N. G. Adams, Some positive ion reactions with H₂: Interstellar implications, Mon. Not. R. Astron. Soc. 197, 377 (1981).
- [12] R. Plašil, S. Rednyk, A. Kovalenko, T. D. Tran, Š. Roučka, P. Dohnal, O. Novotný, and J. Glosík, Experimental study on CH⁺ formation from doubly charged carbon and molecular hydrogen, Astrophys. J. **910**, 155 (2021).
- [13] D. Gerlich, Ion-neutral collisions in a 22-pole trap at very low energies, Phys. Scr. **T59**, 256 (1995).
- [14] D. Gerlich, P. Jusko, Š. Roučka, I. Zymak, R. Plašil, and J. Glosík, Ion trap studies of $H^- + H \rightarrow H_2 + e^-$ between 10 and 135 K, Astrophys. J. **749**, 22 (2012).
- [15] I. Zymak, M. Hejduk, D. Mulin, R. Plašil, J. Glosík, and D. Gerlich, Low-temperature ion trap studies of $N^+({}^{3}P_{ja}) + H_2(j) \rightarrow NH^+ + H$, Astrophys. J. **768**, 86 (2013).

- [16] D. Mulin, Š. Roučka, P. Jusko, I. Zymak, R. Plašil, D. Gerlich, R. Wester, and J. Glosík, H/D exchange in reactions of OH⁺ with D₂ and of OD⁺ with H₂ at low temperatures, Phys. Chem. Chem. Phys. **17**, 8732 (2015).
- [17] K. M. Aggarwal and F. P. Keenan, Energy levels, radiative rates and electron impact excitation rates for transitions in C III, Mon. Not. R. Astron. Soc. 450, 1151 (2015).
- [18] D. Gerlich and S. Horning, Experimental investigation of radiative association processes as related to interstellar chemistry, Chem. Rev. 92, 1509 (1992).
- [19] J. Glosík, P. Hlavenka, R. Plašil, F. Windisch, D. Gerlich, A. Wolf, and H. Kreckel, Action spectroscopy of H_3^+ and D_2H^+ using overtone excitation, Philos. Trans. R. Soc. A **364**, 2931 (2006).
- [20] P. Jusko, O. Asvany, A.-C. Wallerstein, S. Brünken, and S. Schlemmer, Two-Photon Rotational Action Spectroscopy of Cold OH⁻ at 1 ppb Accuracy, Phys. Rev. Lett. **112**, 253005 (2014).
- [21] R. Plašil, I. Zymak, P. Jusko, D. Mulin, D. Gerlich, and J. Glosík, Stabilization of H⁺ H₂ collision complexes between 11 and 28 K, Philos. Trans. R. Soc. A **370**, 5066 (2012).
- [22] D. Hauser, S. Lee, F. Carelli, S. Spieler, O. Lakhmanskaya, E. S. Endres, S. S. Kumar, F. Gianturco, and R. Wester, Rotational state-changing cold collisions of hydroxyl ions with helium, Nat. Phys. 11, 467 (2015).
- [23] E. Endres, G. Egger, S. Lee, O. Lakhmanskaya, M. Simpson, and R. Wester, Incomplete rotational cooling in a 22-pole ion trap, J. Mol. Spectrosc. 332, 134 (2017).
- [24] M. Nötzold, S. Z. Hassan, J. Tauch, E. Endres, R. Wester, and M. Weidemüller, Thermometry in a multipole ion trap, Appl. Sci. 10, 5264 (2020).
- [25] S. Roučka, S. Rednyk, A. Kovalenko, T. D. Tran, R. Plašil, Á. Kálosi, P. Dohnal, D. Gerlich, and J. Glosík, Effect of rotational excitation of H₂ on isotopic exchange reaction with OD⁻ at low temperatures, Astron. Astrophys. **615**, L6 (2018).
- [26] S. D. Price, Interactions of molecular doubly charged ions with atoms, molecules and photons, J. Chem. Soc., Faraday Trans. 93, 2451 (1997).
- [27] M. Tichý, A. Rakshit, D. Lister, N. Twiddy, N. Adams, and D. Smith, A study of the reactions of the ground and metastable states of C⁺, N⁺, S⁺ and N²⁺ at 300 K, Int. J. Mass Spectrom. Ion Phys. **29**, 231 (1979).
- [28] M. Bacchus-Montabonel and Y. Tergiman, Charge transfer rate coefficients in collision of C²⁺ ions with CO and N₂ molecular targets, Chem. Phys. Lett. **497**, 18 (2010).
- [29] T. Su and W. J. Chesnavich, Parametrization of the ion-polar molecule collision rate constant by trajectory calculations, J. Chem. Phys. 76, 5183 (1982).
- [30] L. S. Petralia, A. Tsikritea, J. Loreau, T. P. Softley, and B. R. Heazlewood, Strong inverse kinetic isotope effect observed in

ammonia charge exchange reactions, Nat. Commun. 11, 173 (2020).

- [31] T. Uzer and W. Miller, Theories of intramolecular vibrational energy transfer, Phys. Rep. **199**, 73 (1991).
- [32] J. E. Gambogi, R. P. L'Esperance, K. K. Lehmann, B. H. Pate, and G. Scoles, Influence of methyl group deuteration on the rate of intramolecular vibrational energy relaxation, J. Chem. Phys. 98, 1116 (1993).