Temperature dependence of ternary rate coefficients for the $(CO)_{n-1}^{+}$ $+2CO \rightleftharpoons (CO)_n^{+} + CO$ reaction, and the role of isomers for the growth of larger $(CO)_n^{+}$ clusters

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Ternary rate coefficients for the title reaction have been measured using a rf 22-pole ion trap in the temperature range 65–300 K. For the formation of dimers, the ternary rate coefficient, k_3, follows the power law 2.3×10^{-28} cm⁶/s $\times (300 \, K/T)^m$, with $m = 1.6 \pm 0.2$ over the full temperature range of the experiment. This result is in good agreement with previous measurements at higher temperatures and also with theoretical predictions. The formation of trimers is represented by $k_3 = 1.3 \times 10^{-29}$ cm⁶/s $\times (300 \, K/T)^m$, with $m = 3.2 \pm 0.3$. Including into the evaluation also previously published data measured at higher temperatures, leads to an even steeper temperature dependence. These findings are tentatively explained by the fact that $(CO)_2^{+}$ is a nonlinear molecule with low lying vibrational modes. The formation of tetramers, $(CO)_4^{+}$, is very slow and shows a positive or near zero temperature dependence. This behavior is explained by the presence of two isomers. In order to pass this bottleneck and to reach $(CO)_5^{+}$ and larger clusters, up to $(CO)_9^{+}$, a short but intense gas pulse has been injected into the trap. In contrast to previous high pressure studies where $(CO)_6^{+}$ appears to be especially stable, $(CO)_7^{+}$ turns out to be a favored cluster in the 80 K trap experiment. Also this result can be explained by the existence of two isomers, in which four CO molecules are loosely arranged around a strongly bound $(CO)_2^{+}$ or $(CO)_3^{+}$ core. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1451247]

I. INTRODUCTION

The kinetics of the formation and destruction of molecular cluster ions as well as their thermochemical stability has attracted much interest over the past 30 years.[1] Many systems show a strong change of the binding energy as a function of cluster size. Dimers of heteronuclear cations, $(XY)_2^{+}$, are often bound by more than 1 eV as in the case of $(CO)_2^{+}$.[2,3] This dimer can be considered as a molecule rather than a cluster. For larger aggregates the binding energy drops and finally reaches the heat of evaporation of the neutral XY molecule. Thus the nature of the interaction changes from more covalent bonding to van der Waals bonding with increasing cluster size. Due to these reasons the accurate determination of the electronic and vibrational structure of these clusters is a challenge to *ab initio* calculations. Due to the ambivalent electronic nature[3] of $(CO)_2^{+}$ its low lying vibrations are associated with large amplitude motions in its rather deep potential well. For larger clusters such information from theory is lacking. It is an open question whether the coordination of more ligands to a core ion will complicate the situation or whether dynamical restrictions will lead to a more rigid structure. The latter has been found for ionic clusters with, e.g., H_3^{+} or CH_5^{+} as a core ion.[4,5]

Trap experiments can be performed at comparably low pressures; also the temperature can be chosen over a wide range. First cluster experiments in our low temperature traps dealt with the growth and fragmentation of the weakly bound hydrogen cluster ions, H_n^{+} with $n = 3-23$, at 10 K.[6] Measurements of the rate coefficients for ternary association showed a strong influence on the use of p-H_2 and n-H_2. From these results a shell structure of the H_n^{+} clusters has been derived in which the H_3^{+} core surrounded by three H_2 plays an important role. Isotopic fractionation of these clusters was used to learn more about the intracluster dynamics.[7] The exchange of D and D_2 in collisions with D_2 as a target gas confirmed the structural considerations derived previously.

Most experimental work on cluster ions, and $(CO)_n^{+}$ in particular, has been performed using high pressure mass spectrometry[8] or high pressure drift tubes.[9] In view of the small binding energies for the larger clusters collision induced dissociation (CID) upon extraction from the reaction zone has been discussed as a problem of these methods. Investigations on the thermochemical stability of the $(CO)_n^{+}$ cluster ions[8] showed that different isomers can be formed at different temperatures. One group of clusters carries the dimer as a core molecule with additional CO units attached to it with comparably small binding energies. The other group has a covalently bound trimer ion as a core which has
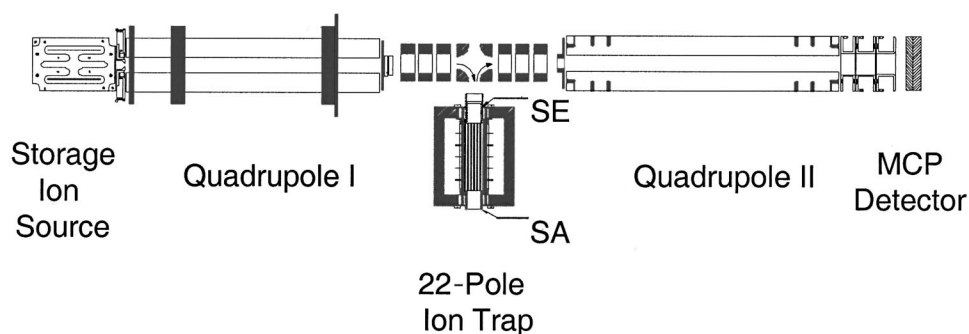
FIG. 1. Cross-sectional view of the ion trap apparatus. The central element is a temperature variable 22-pole ion trap (10–300 K) arranged off axis. Ions are produced in a rf storage ion source, mass selected in quadrupole I and transferred into the trap via a electrostatic quadrupole bender. Product ions are extracted on the same side pulsing the electrode SE. Via the inverted bending field, the ions are injected into quadrupole II for mass analysis. The ions are counted with a MCP detector.

a different structure and is more strongly bound than the trimer of the first group. Both groups are separated by an activation energy. Intracluster isomerization is discussed as an important way to form the more stable species. These dynamical aspects should be visible in the kinetics of growth and fragmentation of the $(CO)_n^+$ cluster ions. One purpose of the present trap experiment is to see how the presence of isomers changes the rate coefficients for ternary association, e.g., as a function of temperature.

For the formation of dimers the temperature dependence of the rate coefficient for ternary growth has been studied in various high pressure experiments in a temperature range from 200 to 500 K since 1970.[9–13] A detailed study on the influence of rotational and translational energy in associative $CO^+ + CO$ collisions has been carried out in Ref. 14. In this investigation it has been confirmed that the total energy is a measure for the lifetime of the $(CO)_2^+$ collision complex. The formation of $(CO)_3^+$ has only been studied around 200 K (Ref. 13) and around 300 K (Refs. 13, 15) and for larger clusters only thermodynamic data from high pressure studies are available.

In the present contribution, detailed experiments following the growth of clusters up to $(CO)_5^+$ are presented. In addition, a way is shown for accelerating the first steps of growth in order to get access to larger clusters. This paper is organized as follows. After a short description of the trapping method a short reminder of the kinetics of ternary association is given. The conventional treatment is modified to allow for the presence of different isomers which grow at different rates. In the Results, emphasis is put on the temperature dependence of the association process. In the Discussion, the present findings are compared to previous experimental results and to results from statistical phase space calculations. The role of molecular vibrations and rotation as well as intracluster isomerization is discussed, too. In the Conclusion, possible future experiments are explained which could probe the spontaneous or collision induced isomerization of the clusters.

II. EXPERIMENT

The experimental setup used in the present study is shown schematically in Fig. 1. The central part of this appa-

ratus is a temperature variable rf 22-pole ion trap designed for the investigation of low temperature ion molecule collisions. A thorough description of the trapping technique can be found in Ref. 16 and first applications to cluster experiments have been published in Ref. 17. In brief, primary CO^+ ions are produced by electron bombardment in a storage ion source. In this way primary ions with thermal kinetic and internal energies can be formed. A train of ions is extracted from the source and mass selected in the first quadrupole (quadrupole I). In order to fill the trap they are deflected by a static quadrupole field and let in through the SE gate electrode. This gate is closed after the pulse of ions turns around at the other gate electrode (SA) and before they can exit from the trap at SE. Radial confinement of the ion cloud is achieved by the rf multipole field of the 22-pole and axial confinement by the gate electrodes. In contrast to the previously described 22-pole apparatus[17] in the present setup the axis of the trap is oriented perpendicularly to the main axis of the apparatus in order to allow direct injection of a molecular beam of condensable gases or radicals into the trap. This new feature has been applied in an experiment where chemical probing is used to determine the rate coefficient for the fine-structure transition $Ar^+({}^2P_{1/2} \rightarrow {}^2P_{3/2})$ in collisions with He and the lifetime of the excited state.[18]

In the present experiment, the neutral CO reactant gas[19] is let in via a precooled tubing into the chamber surrounding the trap. Upon collisions with this gas the primary ions are cooled down rapidly to the wall temperature. The trap is mounted to a closed cycle refrigerator which can be cooled down to 10 K. After the filling and cooling procedure the ion cloud is stored for a variable time (ms up to min) inside the trap. The trap contents is extracted afterwards by a pulse to gate electrode SE and deflected into the second quadrupole (quadrupole II) for mass analysis. The number of trapped parent and product ions is determined via a conventional ion counting detector employing two micro channel plates in Chevron arrangement, a fast tenfold preamplifier and a discriminator. For the determination of the kinetics of the clustering reaction the procedure *ion formation/trapping and reaction/analysis* is repeated many times for typically ten different storage times and for each product mass.

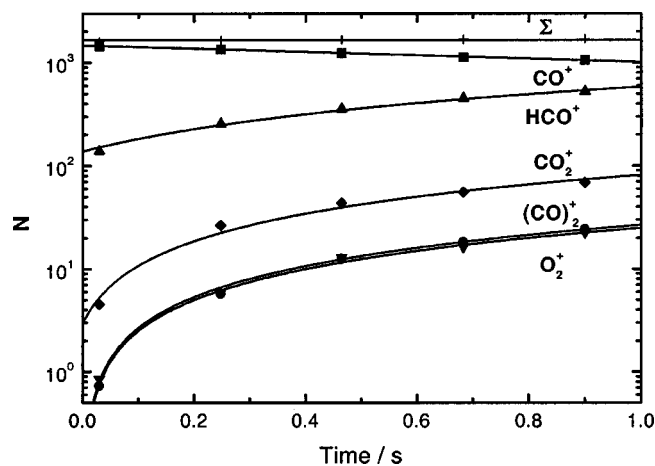Figure 2 shows a result of such a trap experiment for

FIG. 2. Temporal evolution of initially stored CO^+ ions at $T = 180$ K and at a number density $[CO] = 1.2 \times 10^{13}$ cm^{-3}. Four products are detected in this measurement, HCO^+ in reaction with traces of residual H_2, CO_2^+, and $(CO)_2^+$ in reaction with CO and O_2^+ in CT with residual O_2 in the trap. No other important reactions take place as indicated by the constant sum (Σ) of all ions. First order rate coefficients are derived from such measurements by solving and fitting the adequate rate equation system (solid lines).
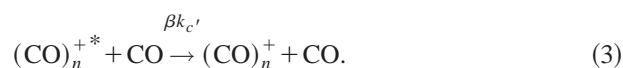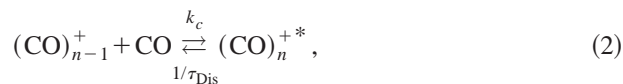
initially stored CO^+ ions at a temperature of 180 K and a CO number density of 1.2×10^{13} cm^{-3}. Over the period of 1 s the number of primary ions drops exponentially (linear decrease in the semilogarithmic plot of Fig. 2) while HCO^+ and CO_2^+, $(CO)_2^+$, and O_2^+ are increasing in number. The sum of all ions in the trap is constant showing that in this measurement all important product channels including those from reactions with background gas have been accounted for. Despite the fact that contaminations of the CO gas are only on the 10^{-6} range, HCO^+ is the dominant product and formed in collisions with residual H_2 ($n = 2.0 \times 10^8$ cm^{-3}). CO_2^+ products are due to collisions with CO_2 ($n = 5.8 \times 10^7$ cm^{-3}), whereas O_2^+ is formed via charge transfer in collisions of CO^+ with O_2 ($n = 1.6 \times 10^8$ cm^{-3}). $(CO)_2^+$ is formed in ternary collisions with the CO target gas. From this experiment the rate coefficient for three body association has been determined to be 6×10^{-28} cm^6/s. In most measurements the number densities of the background gas were lower and the CO number density has been chosen higher in order that cluster formation is a dominant channel and that growth to clusters larger than $(CO)_2^+$ can be observed. In the following a scheme for the kinetics of the ternary association of the $(CO)_n^+$ cluster ions is presented.

III. KINETICS MODELS

The kinetics of the ternary association is described by the simple reaction scheme,

$$(CO)_{n-1}^+ + 2CO \underset{k_{f,n}}{\overset{k_{g,n}}{\rightleftarrows}} (CO)_n^+ + CO. \tag{1}$$
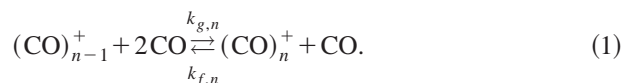
Here $k_{g,n}$ is the apparent binary rate coefficient of the growth reaction, and $k_{f,n}$ that of the fragmentation reaction. In order to obtain some detail on the elementary reaction steps, the three body ion molecule reaction from $(n-1)$ to n is modeled in a two step mechanism,

$$(CO)_{n-1}^+ + CO \underset{1/\tau_{Dis}}{\overset{k_c}{\rightleftarrows}} (CO)_n^{+*}, \tag{2}$$

$$(CO)_n^{+*} + CO \overset{\beta k_{c'}}{\rightarrow} (CO)_n^+ + CO. \tag{3}$$

In the first step, a long lived complex $(CO)_n^{+*}$ is formed; in the second step this complex is either stabilized by an inelastic collision with another CO molecule or by a switching reaction. The apparent binary rate coefficient for growth, $k_{g,n}$, is then given by

$$k_{g,n} = k_{r,n} + k_{3,n}[CO], \tag{4}$$

with $k_{r,n}$ the rate coefficient for radiative association and $k_{3,n}$ the coefficient for ternary association. According to the detailed derivation of the kinetics equations for cluster growth given in our previous paper on the formation of hydrogen cluster ions[6] in the low pressure limit ($1/\tau_{Dis} \gg k_{c'}[CO]$) the ternary rate coefficient is given by

$$k_3 = k_c \cdot k_{c'} \cdot \beta \tau_{Dis}, \tag{5}$$

where k_c and $k_{c'}$ are the collision rate coefficients for reactions (2) and (3), which are approximated by the Langevin rate coefficients ($k_L = 8.7 \times 10^{-10}$ cm^3/s). β is the stabilization efficiency and τ_{Dis} is the effective lifetime of the collision complex. In cases where the intermediate collision complex is a stable molecule with a bond energy D_0 much larger than the collision energy, $E_{col} \approx 3/2\ kT$, almost every collision stabilizes the excited complex, i.e., $\beta \approx 1$. In these cases k_3 is a direct measure of the lifetime τ_{Dis} of the collision complex.

In the present paper the temperature dependence of the ternary rate coefficients for the first two steps of cluster growth is determined. It has been shown empirically that the negative power law,

$$k_3 = cT^{-m} \tag{6}$$

describes quite good the shortening of the lifetime τ_{Dis} with increasing temperature. Statistical models have been developed by Bates[20] and Herbst[21] using phase space theory that predict the power $m = i/2 + \delta$, where i is the total number of rotational degrees of freedom of the reactants and δ is a parameter to account for the temperature dependence of the stabilization efficiency, β. These theoretical approaches have shown to compare favorably with experimental results for many termolecular association reactions.[22] For reactant molecules with low frequency vibrational modes, as is the case for several $(CO)_n^+$ cluster ions, also these degrees of freedom contribute to the phase space available to the reactants when the activated complex $(CO)_n^{+*}$ is dissociating back to the reactants. The vibrational partition function is also strongly dependent on the temperature, thus the temperature dependence of k_3 often becomes even steeper than predicted by Eq. (6). It is one aspect of this work to see how the experimental temperature dependence fits to the simple model behavior.

In the presence of isomers which are characterized by different bond energies, different lifetimes and stabilization efficiencies, different ternary rate coefficients have to be con-
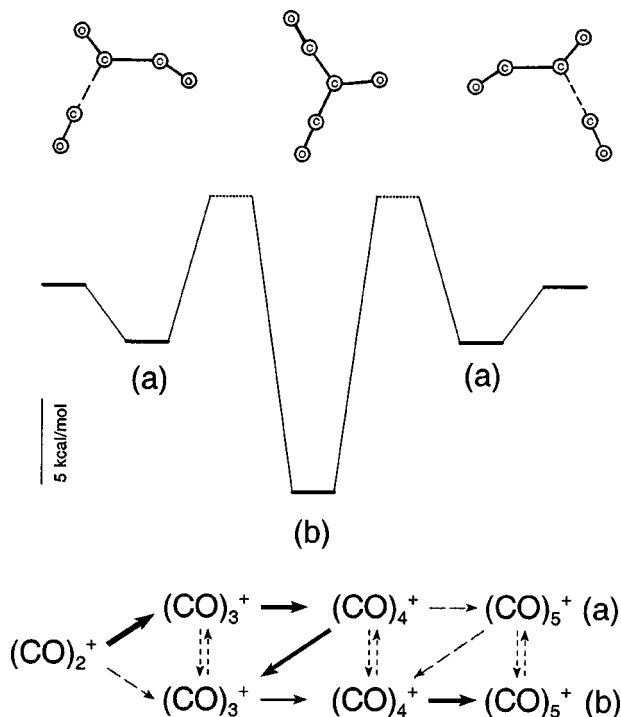
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Growth of $(CO)_n^+$ clusters   4511

5 kcal/mol

FIG. 3. Illustrated is the kinetics of $(CO)_n^+$ cluster growth in the presence of two groups of isomers. The potential energy diagram indicates that the two different isomers (a) and (b) have different binding energies and are separated by a large barrier. The diagram in the lower part indicates schematically various reaction pathways. The possible routes marked by arrows are cluster growth, isomerization and isomerization followed by decay. Bold arrows indicate the pathways we propose for low temperature collisions ($E_A \gg kT$). Thin or dashed arrows indicate pathways which become relevant at higher temperatures as has been shown previously for $(CO)_5^+$ (Ref. 8).

sidered in a more realistic, complex treatment of the kinetics. For larger $(CO)_n^+$ clusters, $n > 2$, several stable isomers have been predicted by *ab initio* quantum chemical calculations.[8] Their presence has to be incorporated in a complete description of the kinetics. According to the MO calculations all isomers fall into two groups which main difference lies in two different core ions, the dimer or the trimer with covalent bonds. Figure 3 shows a schematic potential energy diagram for the $(CO)_3^+$ cluster, where (a) denotes the cluster with $(CO)_2^+$ as a core and (b) the one with $(CO)_3^+$ as a core. In the following it is assumed that in the case of $(CO)_3^+$ the more loosely bound species (a) is separated from the more strongly bound species (b) by a barrier as depicted in Fig. 3. In low temperature collisions only species $(CO)_3^+$ (a) are formed due to this barrier. This route of cluster formation is shown by the bold arrow in the first step of the kinetics scheme in the lower part of Fig. 3. Depending on the actual barrier heights for the specific cluster size and the temperature, isomerization (a) to (b) is possible as indicated by the up/down arrows in the scheme. In fact in a high pressure mass spectrometry study[8] it has been found that $(CO)_5^+$ (a) isomerizes with an excess energy which is sufficient to break up the cluster to yield $(CO)_4^+$ (b) as a product. This step in the kinetics is depicted in the scheme as a dashed arrow pointing down-backwards. The complete kinetics for larger $(CO)_n^+$ clusters as shown in Fig. 3 appears rather complicated due to the isomerization problem. The thickness of the arrows indi-
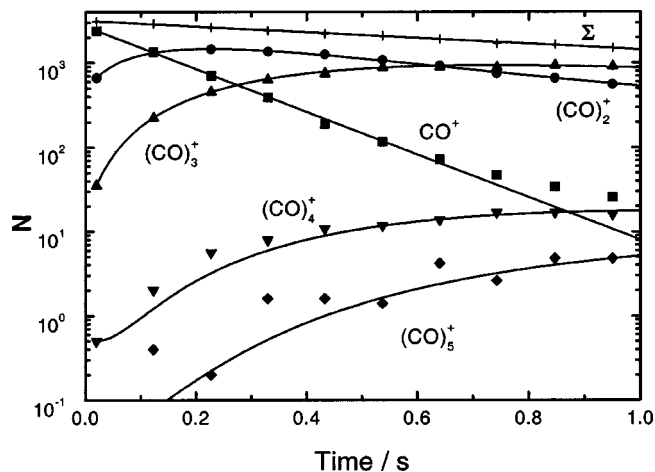

FIG. 4. Cluster growth upon storage of CO^+ primary ions at $T = 80$ K and at a number density $[CO] = 4.4 \times 10^{13}$ cm^{-3}. While $(CO)_2^+$ and $(CO)_3^+$ grow very rapidly and become dominant, $(CO)_4^+$ and $(CO)_5^+$ appear much slower. Corresponding smaller ternary rate coefficients, see Table I, are indicative for smaller binding energies of the latter species.

cates the probability of the proposed pathway for the cluster growth in the present trap experiment around 80 K as it will be derived from the experimental results and their discussion below.

As a starting point for understanding the kinetics the experimental data have been analyzed using only one set of rate coefficients for each cluster size and each particular temperature. In this approach the presence of isomers or the appearance of isomerization will be seen as the bad quality fitting of the temporal evolution of the ion cloud with a single set of rate coefficients and/or by the temperature dependence of the ternary rate coefficients.

IV. RESULTS

Figure 4 shows an example of the cluster growth at $T = 80$ K and at a number density of $[CO] = 4.4 \times 10^{13}$ cm^{-3}. This measurement demonstrates the large dynamic range (more than four orders of magnitude in the number of ions) which can be covered in a trap experiment. In this example, $(CO)_2^+$ and $(CO)_3^+$ become the dominant ions in the trap. Already within the first 100 ms, 50% of the number of CO^+ ions are converted into dimers which grow subsequently to $(CO)_3^+$. The formation of $(CO)_4^+$ and $(CO)_5^+$ is much slower such that these two ions make up only about 1% of all ions after a storage time of 1 s. The ternary rate coefficient for growth of $(CO)_4^+$ is much smaller than the corresponding values for the first two reaction steps.

TABLE I. Ternary rate coefficients, $k_{3,n}$, for the formation of $(CO)_n^+$ cluster ions, $n = 2-5$ at $T = 80$ K. τ_{Dis} are the lifetimes of the collision complexes [see Eq. (5)] and $k_{f,n}$, the rate coefficients for fragmentation.

n	$k_{3,n}/(10^{-27}$ cm^6/s)	τ_{Dis}/ps	$k_{f,n}/(10^{-14}$ cm^3/s)
2	2.6	3930	$\cdots$
3	1.0	1851	1.8
4	0.042	85	5.6
5	0.38	812	0.68
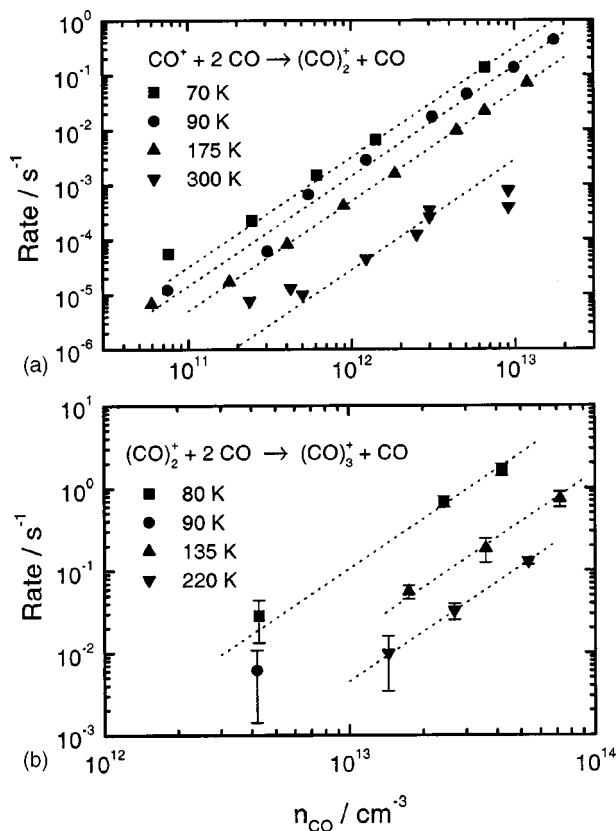
FIG. 5. Density dependence of the rate for ternary association. (a) CO^+ + 2 CO, at $T = 70$ K (■), 90 K (●), 175 K (▲), and 300 K (▼). (b) $(CO)_2^+$ + 2 CO at 80 K (■), 90 K (●), 135 K (▲), and 220 K (▼). Dashed lines represent fits to the expected $[CO]^2$ dependence. Corresponding ternary rate coefficients, $k_{3,n}$, derived from these fits are displayed in Fig. 6 as a function of temperature.

FIG. 6. Temperature dependence of the ternary rate coefficients for the formation of dimers (■,□) and trimers (●,○). Bold symbols correspond to results from a full simulation of the set of coupled rate equations as described in the text. Hollow symbols show results from a fit of the growth rate as shown in Fig. 5. Data points from previous work for trimers (▼) are summarized in Table II. Straight line fits refer to a power law dependence, $k_3 \sim T^m$, with $m = 1.6$ and 3.2 for $n = 2$ and 3, respectively.

The solid lines in Fig. 4 represent a solution of the set of coupled rate equations according to the simple kinetics model accounting only for one isomer. The agreement between this model kinetics and the experimental data is excellent for CO^+, $(CO)_2^+$, and $(CO)_3^+$ but shows significant deviations for $(CO)_4^+$ and $(CO)_5^+$. In the case of $(CO)_4^+$ obviously more ions are formed at early times. This deviation cannot be reduced by modifying the parameters entering the simple growth model described by Eq. (1). We take this as an indication that the $(CO)_4^+$ products are indeed produced via (at least) two different processes under the conditions prevailing in our trap. This observation will be discussed below in more detail.

The ternary rate coefficients, $k_{3,n}$, derived from fitting the simple kinetics for cluster sizes $n = 2-5$, are summarized in Table I together with the rate coefficients for fragmentation, $k_{f,n}$. Included are also the complex lifetimes, τ_{Dis}, which have been derived from $k_{3,n}$ using Eq. (5) with the assumption $\beta = 1$. These lifetimes are in the nanosecond and subnanosecond range. In comparison the time between collisions is rather long, ≈ 30 μs. Thus even for the longest complex lifetime the chance to form a stable cluster is rather low, $< 10^{-4}$.

The fragmentation rate coefficients for the clusters $n = 2-5$ presented in Table I are rather small compared to the Langevin rate coefficient. Therefore the chance to break a
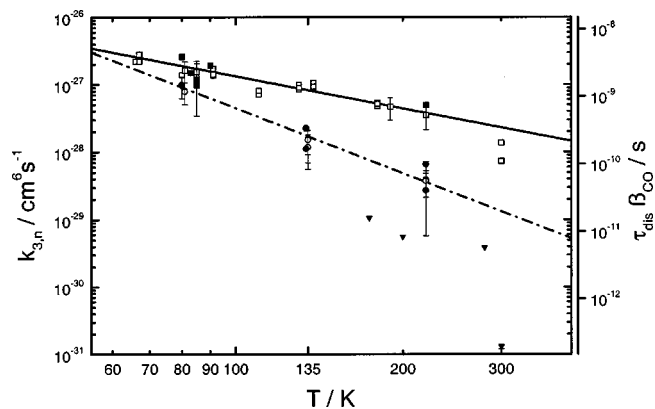
cluster in a thermal collision is small too. Thus the $(CO)_n^+$ cluster ions appear to be strongly bound with respect to the thermal collision energies of the trap experiment. For the smallest cluster, $(CO)_2^+$, this is very well known and the large binding energy results in such a very small rate for fragmentation that due to the limited sensitivity of our experiment it is hard to give an upper limit for this rate coefficient. On the contrary $(CO)_4^+$ has the largest fragmentation rate which indicates that the binding energy is smaller than compared to the neighboring clusters.

In order to determine the pressure and temperature dependence of the ternary rate coefficients a variety of measurements have been performed between 65 K and 300 K and for various CO target densities. In Fig. 5 the rates of formation of $(CO)_2^+$ and $(CO)_3^+$ are plotted as a function of the target density. In this double logarithmic plot the values for each temperature fall on a straight line with a slope 2. Thus the apparent rate is proportional to the square of the CO number density, $[CO]^2$, as expected for ternary association processes. This is a proof of the assumption made for the preliminary determination of the rate coefficients for ternary association. Minor deviations from this dependence can be seen for the formation of $(CO)_2^+$ at low CO densities for several temperatures. Here the rates are slightly larger than given by the straight line. As can be seen from Eq. (4), radiative association can play a role at such low densities. Therefore some information on $k_{r,n}$ can be extracted. The rate of 5×10^{-5} s^{-1} measured at 70 K and at a density of 8×10^{10} cm^{-3} leads to an upper limit $k_{r,n}(CO)_2^+ < 6 \times 10^{-16}$ cm^3/s. For $(CO)_3^+$ no deviation from the linear decrease is obvious, indicating that ternary association still prevails. Therefore one only can conclude that the data are consistent with $k_{r,n}(CO)_3^+ < 8 \times 10^{-15}$ cm^3/s.

The ternary rate coefficients derived from the measurements shown in Fig. 5 are displayed in Fig. 6 as a function of temperature. In the double logarithmic representation, the rate coefficients for the formation of $(CO)_2^+$ and $(CO)_3^+$ fall on straight lines with negative slopes. Thus their temperature

TABLE II. Summary of the ternary rate coefficients, k_3, for the growth of dimers, trimers, and tetramers at a given temperature. In cases where the exponent, m, for the power law dependence according to Eq. (7) is available, k_3 is given for $T = 300$ K, and column 4 represents the temperature range of the corresponding experiment.

System	$k_3/10^{-29}$ $cm^6\,s^{-1}$	Exponent m	T/K	p/Torr	Method/ Reference
$CO^+ + CO$	14.3	⋯	340	0.2–1.2	HPMS[a]/11
	11.0–13.5	⋯	300	0.08–0.16	DS[b]/10
	19.8	1.5	120–650	0.15–1.01	HPPS[c]/12
	10.7, 7.6, 11.2	⋯	174, 200, 280	35	DS/13
	13.3	3.3±0.2	365–530	0.5–3	HPPS/
	12	1.5±0.30			HPPS/9
	24	1.54±0.35			DS/9
	19.7±0.3	1.6±0.1	350–550	5	DS/9
	23	1.6	65–300	1×10^{-6}–4×10^{-4}	rf-trap This work
$(CO)_2^+ + CO$	1.06, 0.56, 0.39	⋯	174, 200, 280	35	DS/13
	>0.012	⋯	295	0.01–0.5	HPMS/15
	1.3	3.2	80–220	6×10^{-5} -1.5×10^{-3}	rf-trap This work
$(CO)_3^+ + CO$	0.61	⋯	174	35	DS/13
	4.0	⋯	80	7×10^{-5}	rf-trap This work

[a]HPMS, high pressure mass spectrometry.
[b]DS, drift source.
[c]HPPS, high pressure pulsed source.

dependence as well as that for $\tau_{Dis}\,\beta$, see right axis of Fig. 6, is well represented by the power law given in Eq. (6). Best fit results of the present study for $k_3(300\text{ K})$ and the exponent m for the form,

$$k_3(T) = k_3(300\ \text{K})(300\ \text{K}/T)^m \qquad (7)$$

are given in Table II. For the formation of dimers a similar behavior has been found by several authors[9–13] as can be seen in the comparison shown in Table II. While there are larger differences in the absolute value for $k_3(300\text{ K})$ the agreement in the exponent is rather good where available. In the present work the temperature range has been significantly extended to lower temperatures and rate coefficients were obtained under low pressure conditions. A comparison to theoretically expected values will be discussed below.

For the formation of trimers only two groups[13,15] determined rate coefficients in the range from 175 K to 300 K and for high pressures. Again the absolute values for $k_3(300\text{ K})$ differ quite a bit and an exponent for the temperature dependence is not available (see Table II). In this work the temperature range has been extended down to 80 K and the exponent m has been determined to be 3.2, twice as high as for the first reaction step. Also one data point is available in the literature for the growth of tetramers (see also Table II).[13] The absolute value is one order of magnitude smaller than in the present work. However, due to the large difference in temperature these values are hard to compare because the temperature dependence for this step is unknown. Due to the low pressures of the present experiment it is hard to follow the growth of larger clusters at higher temperatures. However, the formation of $(CO)_4^+$ has been seen also at $T = 135$ K and k_3 appears to be similar if not larger, ($\approx 10^{-27}\ cm^6/s$) than for $T = 80$ K ($\approx 4\times10^{-28}\ cm^6/s$, see Table I). Such a positive temperature dependence is unex-

pected for a simple sequential cluster growth ($n-1\rightarrow n\rightarrow n+1$). However, in the case of $(CO)_n^+$ cluster ions the presence of (at least) two isomers could explain such a behavior as will be discussed in the following section.

The ternary growth of $(CO)_4^+$ is exceptionally slow even at $T = 80$ K. Therefore it is hard to follow the formation of larger $(CO)_n^+$ clusters. One way to overcome this problem is to use a very high number density at the beginning of the trapping period. Such experiments have been performed using a pulsed gas inlet in a ring electrode trap setup.[23] Figure 7 shows a result of this experiment. The whole ion cloud is extracted from the trap and simultaneously mass analyzed employing a linear time-of-flight arrangement. During the
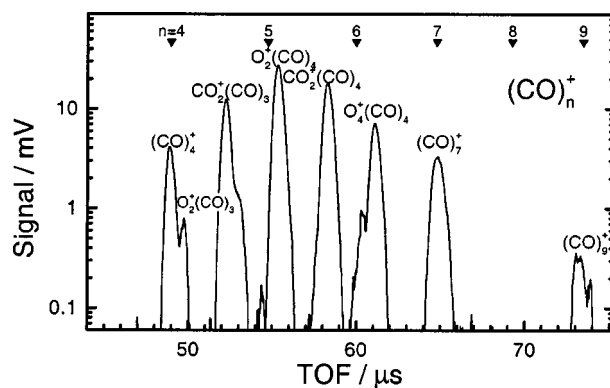

FIG. 7. Time-of-flight mass spectrum of $(CO)_n^+$ cluster ions. Using a high intensity gas pulse of CO, larger clusters, $n = 4$–9, are formed at $T = 80$ K in a ring electrode trap experiment (Ref. 23). The trap content is mass analyzed after a storage time of 2 s in this case. Due to the parent ion production in the trap and due to the high CO number density also clusters with different core ions are present. Ticks (▼) atop the spectrum indicate flight times for $(CO)_n^+$ cluster ions. Noticable is the comparably large number of $(CO)_7^+$ clusters and the lack of $(CO)_8^+$ in this spectrum.

gas pulse, CO number densities higher than $10^{15}\,\text{cm}^{-3}$ are obtained and clusters up to $(CO)_9^+$ are detected. Due to the ion preparation in the trap and the high intensity gas pulse several more species than just the $(CO)_n^+$ cluster ions are formed in this preliminary measurement as can be seen in Fig. 7. However, one clear result concerning the growth of larger clusters is found too. While $(CO)_8^+$ is absent in the spectrum, $(CO)_7^+$ is a dominant CO cluster ion species. Thus $(CO)_7^+$ appears as a comparably strongly bound cluster. This is in contradiction to previous findings in high pressure experiments[8] where $(CO)_6^+$ has been found to have this role.

V. DISCUSSION

In the present work the kinetics of $(CO)_n^+$ cluster formation has been studied in great detail under low pressure conditions over a wide range of temperatures, in particular reaching low temperatures where kinetic data are missing. Several new results concerning the temperature dependence of the ternary rate coefficient, the presence of $(CO)_n^+$ isomers in the trapped ion cloud, and the route to larger cluster ions, $n \geq 4$ have been obtained. However, also many open questions, e.g., on the electronic and vibrational structure as well as on the barriers separating the isomers arise from these studies.

Ternary rate coefficients for the growth of $(CO)_2^+$ and $(CO)_3^+$ follow the negative power law dependence presented in Eq. (6). For $(CO)_2^+$ the exponent $m = 1.6$ agrees rather well with previous experimental data as well as with the theoretically expected value $m = 2$. In the present case CO^+ and CO have two rotational degrees of freedom each, which results in $m = 2$ for the formation of dimers. The small deviation of the experimental values is discussed in Ref. 9 to be a pressure effect. At high pressures when association is happening close to collision rate, association and thermalization are at competition thus the growth rates can be effected by a modified rotational population of the clusters leading to an erroneous temperature dependence. In fact all methods listed in Table II except the present one use comparably high pressures. Therefore a common deviation from the correct temperature dependence can not be ruled out. In contrast in the present experiment this effect has been ruled out since the rate of dissociation, $1/\tau_{Dis}$, of the collision complex, which has been determined to be about $10^8-10^9\,\text{s}^{-1}$ (see τ_{Dis} in Table I), is much larger than the collision rate, $k_c[CO]$ $< 8.7 \times 10^{-10}\,\text{cm}^3/\text{s} \times 10^{14}\,\text{cm}^{-3} \approx 10^5\,\text{s}^{-1}$. For this reason the rotational population of the reactants is not affected by the association reaction in our trap experiment. However, because of the agreement of all experimental data (Table II) it remains questionable whether such a pressure effect is present in the high pressure mass spectrometry work.

For the first two association steps the temperature dependence of the stabilization efficiency, β, has been neglected as stabilization appears to be much more likely than fragmentation in such a collision due to the strong binding energies of $(CO)_2^+$ and $(CO)_3^+$.[8] The temperature dependence of k_3 for the formation of $(CO)_3^+$ is much steeper than for $(CO)_2^+$. According to the statistical theory the exponent should be 0.5 larger since $(CO)_2^+$ is a nonlinear molecule[8] and thus has

three instead of two rotational degrees of freedom. However, this increase hardly explains why m is twice as large as for the previous association step. In fact when taking into account that previous data for higher temperatures of Horton *et al.*[13] (see Table II) are falling below the line given for the fit to the power law dependence and that our results show larger uncertainties at these higher temperatures, the temperature dependence could be curved and even steeper for higher temperatures than suggested by the simple fit to Eq. (6). Such a curved behavior is expected and has been found in many examples previously[22] when energy cannot only be partitioned to translation and rotation of the reactant molecules but also to vibration. *Ab initio* calculations[24] for $(CO)_2^+$ show vibrational modes well below 200 cm^{-1} which could be responsible for the observed temperature dependence of k_3. In return the steep negative temperature dependence can be taken as evidence for the fact that $(CO)_2^+$ is a nonlinear molecule with low lying vibrational modes.

Besides these detailed experiments on the temperature dependence of the first two association steps of the $(CO)_n^+$ clusters three pieces of evidence have been obtained for the presence of at least two isomers for clusters with $n \geq 3$. (1) The best fit solutions of the set of master equations could not well reproduce the abundance of larger clusters ($n \geq 4$). (2) The rate coefficient for formation of $(CO)_4^+$ shows a zero or slight positive temperature dependence in contrast to the expected negative power law given in Eq. (6). (3) In the present study a magic number, i.e., high abundance, for cluster size $n = 7$ has been found instead of $n = 6$ in previous high pressure studies. This difference can be related to the different core ions $(CO)_3^+$ of the (b) isomer and $(CO)_2^+$ of the (a) isomer. In the following each argument will be discussed in more detail.

It has been shown in Fig. 4 that the number of $(CO)_4^+$ ions produced could not be fitted by the simple sequential reaction model given in Eq. (1). It appears that the evolution of $(CO)_4^+$ shown in Fig. 4 is characterized by a first fast increase which is followed by a slow increase. Such a behavior can be explained with the assumption that the $(CO)_3^+$ clusters consist of two different isomers, as indicated in Fig. 3, which grow at different rates. Therefore we are left with the question how the two isomers are formed. One possible way is depicted in Fig. 3. $(CO)_3^+$ (a) is formed in collisions of the $(CO)_2^+$ precursor with CO and this isomer is separated by a barrier from $(CO)_3^+$ (b). In presence of a high barrier the (b) type isomer cannot be formed in a direct association. In fact it has been shown by Hiraoka *et al.*[8] that this barrier must be higher than the one for the isomerization of larger clusters, namely, $(CO)_5^+$, which has been directly observed in that work only for rather high temperatures. Therefore we speculate that at the temperatures where rapid formation of $(CO)_4^+$ has been observed in this work, $(CO)_3^+$ is formed from $(CO)_2^+$ only in the (a) form. For this reason a different pathway to form $(CO)_3^+$ (b) has to be found.

For a better understanding, the energetics of the involved intermediates and products should be considered. Binding energies of $(CO)_3^+ - (CO)_5^+$ in both isomeric forms and the barrier height for $(CO)_5^{+\#}$ have been taken from Ref. 8 and are shown in Fig. 8. The barrier height for $(CO)_4^{+\#}$ is un-

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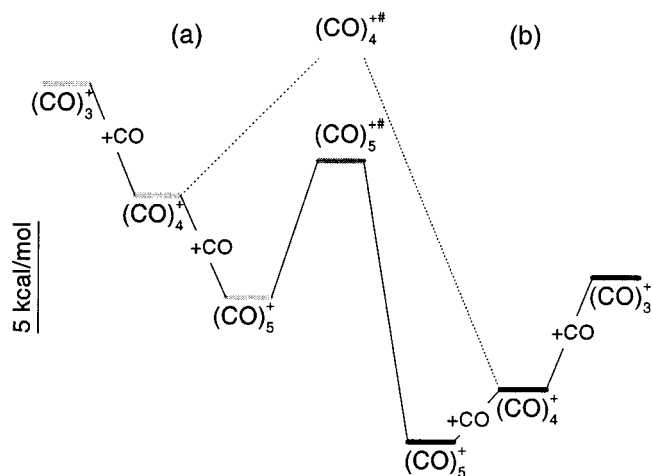
Growth of $(CO)_n^+$ clusters   4515

FIG. 8. Energetics of the lowest (a) and (b) isomers for $(CO)_n^+$, $n = 3-5$, as taken from the calculations of Ref. 8. (a) Isomers are separated from (b) by a proposed barrier $(CO)_n^{+\#}$. Due to the large energy gain by a transition from (a) to (b) isomerization very likely leads to fragmentation of the parent cluster.

One implication of the presence of $(CO)_4^+$ (a) is that the barrier height of $(CO)_4^{+\#}$ should be higher than the one for $(CO)_5^{+\#}$ and/or the densities of states in the area of the transition state should be vastly different in order to explain this behavior. These questions should be answered in a dedicated experiment on the isomerization.

The second experimental result which shows that isomerization plays an important role in the formation of $(CO)_n^+$ clusters is the zero or slight positive temperature dependence for the formation of $(CO)_4^+$. For the sequential growth of cluster ions a negative temperature dependence is expected, see Eq. (6). However, in the presence of a barrier, as depicted in Fig. 8, isomerization proceeds faster at higher temperatures (positive temperature dependence) due to the activation barrier separating (a) and (b) isomers. The two effects largely cancel each other in the temperature range of the present experiment.

The third piece of information on the presence of isomers lies in the magic numbers of larger $(CO)_n^+$ clusters which have been found to differ by one CO unit in the present experiment as compared to the high pressure mass spectrometry work. In view of the different isomers for the smaller clusters, their isomerization for $(CO)_4^+$ and the different experimental conditions, especially the temperatures, it seems quite possible that different magic numbers can be found. Even for much larger clusters it has been suggested by Hiraoka et al. that the clusters still fall into the (a) and (b) category, where (a) clusters are formed in low temperature collisions and (b) originate from (a) via isomerization which requires a sufficiently high temperature. Thus $(CO)_6^+$ and $(CO)_7^+$ may simply relate to the dimer molecule (a) as a core in one case and the trimer (b) as a core in the other case. $(CO)_6^+$ has been studied in the mass spectrometry work at temperatures below the point where isomerisation takes place. Thus $(CO)_6^+$ of the high pressure mass spectrometry study is most likely an (a) type isomer. In the present study $(CO)_7^+$ has been found as a stable species at even lower temperatures. The difference is that in our low density experiment the binding energy of the collision system is available for reaction, see discussion above (Fig. 8), and isomerization occurs even at lower temperatures and at a smaller cluster size. As a consequence $(CO)_7^+$ is most probable a (b) type isomer.

VI. CONCLUSIONS

The formation of $(CO)_n^+$ clusters via ternary association has been investigated in a temperature variable 22-pole trap. The presence of isomers complicates the sequential reaction scheme of Eq. (1). Therefore it has been revised by the more complex pathways given in Fig. 3. All experimental findings are in accordance with this simple scheme and the net pathway which is indicted by the thicker arrows. In order to confirm some of the speculations given in this work more experiments are needed which simply test some of the proposed reaction steps. One experimental problem which has been discussed is the high density which is necessary to form the clusters while no collisions should be taking place for the study of the spontaneous decay of a cluster due to isomer-

known but has been assumed in this graph to be similar to the one in $(CO)_5^{+*}$ in order to illustrate possible pathways. Our discussion starts with the $(CO)_3^+$ (a) isomer which upon collisions with CO can either form a stable $(CO)_4^+$ (a) cluster or isomerize. If isomerization would be a dominant channel at this reaction step no difference in the growth rate of $(CO)_4^+$ would be observable because all $(CO)_4^+$ would be formed by $(CO)_3^+$ (b) isomers.

Considering the next association step, $(CO)_4^+ (a) + CO$, again the formation of stable $(CO)_5^+$ (a) or isomerization is possible. On the one hand, the first process seems to be slow since $(CO)_5^+$ is formed only very slowly at times when $(CO)_4^+$ (a) is present in the trap, see Fig. 4. On the other hand, upon isomerization the system has to get rid of its excitation energy in order to form the next stable cluster. Due to the difference in binding energies and due to the isomerization energy available in the system it appears rather likely that upon isomerization the cluster loses a CO rather than gaining one, e.g., $(CO)_4^+ (a) + CO$ is higher in energy than $(CO)_3^+ (b) + 2CO$. Since isomerzation is not happening in $(CO)_3^+$ and $(CO)_4^+$ is growing with two different rates, we conclude that isomerisation happens in $(CO)_4^+ (a) + CO$ which ends up as $(CO)_3^+$ (b). Due to the presence of $(CO)_4^+$ (a) its formation should be faster than the isomerization. Another hint for this pathway is that $(CO)_4^+$ grows slower, i.e., $(CO)_4^+$ (b), when the formation of $(CO)_5^+$ becomes a visible channel, see Fig. 4. This indicates that $(CO)_5^+$ is formed by one isomer, namely, $(CO)_4^+$ (b), only. According to the energetics given in Fig. 8 ternary association of the other isomer, $(CO)_4^+ (a) + 2CO$, is rather unlikely but isomerization to form $(CO)_3^+$ (b) as discussed in this paragraph prevails. This isomerization of $(CO)_5^+$ (a) has been observed in previous work by Hiraoka et al. at temperatures above 140 K. In that case larger temperatures are necessary for the isomerization because much of the binding energy is taken out of the collision system under the high density conditions.

ization. This particular cluster system is especially suited for the study of isomerization because dissociation products are expected to emerge from this reaction. One way to do such an experiment is the production of clusters in a free jet. This allows the formation of clusters at much lower temperatures, thus probably selecting (a) type clusters only. Using a REMPI scheme for the production of CO^+ the formation of $(CO)_2^+$ as a function of the rotational state of CO^+ has been investigated.[14] With the help of an additional electrical field it is possible to effectively heat the clusters. Such a setup could be used as a source for a low temperature (10 K) trap experiment where the spontaneous or collision induced dissociation of the clusters can be studied. Lifetimes on the order of minutes are accessible with the trapping technique. Isomerization of cold and metastable $(CO)_3^+$ is one of the key experiments that should be done in the future. One way to make the isomerization detectable is chemical probing. An example for this method is the different growth rate to form $(CO)_4^+$ as indicated in this work. Besides this more efficient chemical reactions might be found.

Another interesting possibility lies in the use of IR radiation to excite vibrational modes of the cluster to enhance the isomerization rate and thus also the dissociation rate of particular $(CO)_n^+$ clusters. Absorption frequencies near the free CO stretching vibration add about 0.27 eV (6.2 kcal/mol) to the cluster, even higher values can be supplied exciting overtones or combination bands. Similar to the vibrational predissociation spectroscopy such spectra could be used to learn more about their structure and intramolecular binding. In case of the $(CO)_3^+$ (a) isomer on the one hand this energy is sufficient to dissociate it into $(CO)_2^+ + CO$ while on the other hand it might not be sufficient to overcome the barrier (see Fig. 3) when starting with $(CO)_3^+$ (b). This can be one efficient way to probe the composition of $(CO)_3^+$ isomers. Such results could be a strong motivation for improved theoretical calculations on the system especially on the determination of nonequilibrium structures near the transition states for isomerization.

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