Ion Chemistry of Carbon Dioxide in Nonthermal Reaction with Molecular Hydrogen

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1. INTRODUCTION

Carbon dioxide, CO₂, is one of the trace gases present in the Earth’s atmosphere and is uniformly distributed in its layers. This molecule is also the main component of the Mars and Venus atmospheres,¹,² and it is also present in the interstellar medium as neutral (CO₂) and ionic (CO₂⁺, HCO₂⁺) species.³,⁴ CO₂ and other trace gases such as methane, CH₄, nitrous oxide, N₂O, and water, H₂O, absorb infrared light coming from the Earth’s surface and consequently increase the temperature of the planet, producing the so-called “atmospheric greenhouse effect”. The increase of CO₂ in the atmosphere is also the main factor for the increased acidity of the sea.⁵ The need for rapid reduction of fossil fuel emission and the requirement of “negative CO₂ emissions” are pushing for the development of new approaches and technologies to produce energy (renewable sources)⁶,⁷ and remove CO₂ from the atmosphere (carbon geoengineering).⁸ Indeed, CO₂ conversion into suitable chemicals and fuels such as methanol, formaldehyde, and formic acid is one of the great challenges of the 21st century.⁹ The transformation of CO₂ requires a coreactant that acts as a hydrogen source (like CH₄, H₂O, or H₂) or the splitting of CO₂ into CO and O₂.¹⁰ Among the different emerging and novel technologies for the activation and conversion of CO₂, the plasma-based approach has recently received much attention.¹¹ In this strategy, carbon dioxide is activated by energetic electrons and the experimental conditions are mild, clean, and upscaling. Plasma is an ionized gas containing also neutral species, for example, atoms, molecules, radicals, and excited species that can emit light. All these species create a complex network of chemical reactions that can produce a system of interest for many potential different applications¹² and, in the best cases, used on an industrial scale. The plasma is in “local thermodynamic equilibrium” (LTE) if all the species are at the same temperature (thermal plasma), which is otherwise called nonthermal plasma.¹³ Here, highly energetic electrons can activate the inert carbon dioxide¹⁴ at room temperature, which then can react with species such as CH₄, H₂O, or H₂, leading to an efficient conversion of CO₂ despite the low selectivity in the correspondent products. However, this undesired effect can be overcome by employing plasma catalysis, which can lead to a more selective production of specific compounds.¹⁵ Although there are several setups for the plasma-based CO₂ conversion, the mechanistic insights into CO₂ transformation are not well understood, and this prevents the prediction of a realistic trend on product yields and selectivity. Hence, an accurate experimental and theoretical analysis at the molecular level of the reactions of the “internally excited” CO₂⁺ with these neutrals is undoubtedly relevant.¹⁶⁻²¹ The reaction of carbon dioxide cation with molecular hydrogen has been already studied at low temperatures (15–300 K) under thermal conditions by Gerlich and co-workers.²² Instead, in the present study, we report an experimental and theoretical study of the same reaction with diatomic hydrogen.²³,²⁴ The tunable synchrotron radiation has been used to excite vibrationally the reagent ions and the different internal energy of the carbon dioxide cation: the tunable synchrotron radiation has been used to excite vibrationally the reagent ions and the corresponding products. However, the reaction of carbon dioxide cation with molecular hydrogen has been well studied at room temperature, which then can react with species such as CH₄, H₂O, or H₂, leading to an efficient conversion of CO₂ despite the low selectivity in the correspondent products. However, this undesired effect can be overcome by employing plasma catalysis, which can lead to a more selective production of specific compounds. Although there are several setups for the plasma-based CO₂ conversion, the mechanistic insights into CO₂ transformation are not well understood, and this prevents the prediction of a realistic trend on product yields and selectivity. Hence, an accurate experimental and theoretical analysis at the molecular level of the reactions of the “internally excited” CO₂⁺ with these neutrals is undoubtedly relevant. The reaction of carbon dioxide cation with molecular hydrogen has been already studied at low temperatures (15–300 K) under thermal conditions by Gerlich and co-workers. Instead, in the present study, we report an experimental and theoretical study of the same reaction with different internal energy of the carbon dioxide cation: the tunable synchrotron radiation has been used to excite vibrationally the reagent ions and the experimental results has been analyzed by developing a
2. METHODS

2.1. Synchrotron Experiments. The monochromatized radiation from the beamline CiPo (Circular Polarization) at ELETTRA (Trieste), described in detail in our previous studies,27–30 has been used to produce carbon dioxide radical cations with different internal energies. The beamline, equipped with an electromagnetic elliptical undulator/wiggler, works in the vacuum ultraviolet (VUV) region, and a normal incidence monochromator (NIM) provides photons in the 8–40 eV energy range. The aluminum grating of the NIM, operating in the energy range 8–17 eV and providing a photon flux of about $10^9$–$10^{10}$ photons/s with an energy resolution of about 20–20 meV, has been used. The photon energy was calibrated against the autoionization features observed in the Ar total photoionization cross-section between the 3p spin orbit components.31 The effusive molecular beam of carbon dioxide has been introduced in the ion source through a leak valve and ionized by synchrotron radiation at a pressure of about $10^{-6}$–$10^{-5}$ mbar. The generated CO$_2^+$ ions were guided with several optical lenses into the octupole reaction cell at the nominal collision energy (CE) of 0 eV with an energy spread of about 150 meV. This value has been obtained by measuring the CO$_2^+$ yield as a function of the retarding field at the entrance of the octupole. The reactants H$_2$ or D$_2$ were inserted into the reaction cell (octupole) at different nominal pressures from 9.0 × $10^{-6}$ to 9.0 × $10^{-5}$ mbar and at room temperature. Mass spectra in the mass over charge (m/z) range 10–48 were acquired at 14.0 eV photon energy without and with neutral gases in the reaction cell at the nominal pressures of 9.0 × $10^{-6}$ and 3.0 × $10^{-5}$ mbar and with acquisition time ranging from 1 to 5 s/p. The data on the main signals acquired at m/z = 44 (CO$_2^+$), 45 (HCO$_2^+$), and 46 (DCO$_2^+$) were fitted by Gaussian profiles with the OrignPro 2015 software to evaluate the isotopic effect. The intensities of the reagent and product ions in the ion-molecule reactions of CO$_2^+$ with H$_2$ or D$_2$ were measured by scanning the photon energy in the range of 13.7–15.0 eV with a step of 0.10 eV and an acquisition time of 30 s/point at several pressure values in the reaction cell, namely, 0.9 × $10^{-5}$, 1.2 × $10^{-5}$, 3.0 × $10^{-5}$, 6.0 × $10^{-5}$, and 8.6 × $10^{-3}$ mbar. The pressure measurements are affected by an error of about 30%. For the sake of clarity, the ' in CO$_2$ is omitted in the following sections.

2.1.1. Materials. All the samples were used at room temperature. Carbon dioxide CO$_2$ was from SIAD with purity >99.99%. The H$_2$ and D$_2$ gases were purchased from Sigma-Aldrich with purity >99.99% and with a 99.8 atom % D.

2.2. Theoretical Calculations and Methodology.

2.2.1. Reactive Potential Energy Surface. The interaction between the ionized CO$_2^+$ and the neutral hydrogen molecule has been studied by means of ab initio calculations based on density functional theory (DFT) double-hybrid approach, which takes into account the radical nature of the species during the reaction. The functional used throughout all the calculations is the B2PLYP of Grimme,32 and the basis set is the valence double-zeta Pople polarization and diffuse functions 6-31++G**.33 All the frequency calculations have been carried on in the harmonic approximation. The electronic structure calculations have been done using the Gaussian code.34 The accuracy of the calculation has been verified by comparing the reaction enthalpy of 121.36 kJ/mol with the theoretical value of 121.9 kJ/mol obtained in this work. The open shell radical nature of the present reaction is properly accounted for with the employed level of calculation, as shown by the partial charge and spin analysis presented in the next section. The reactive potential energy surface (PES) has been calculated by scanning both the O–H and H–H coordinates with a variable step whose minimum value has been taken as 0.02 Å in the regions near the reactive complex. During the scan, all the other geometrical coordinates, except the scanning ones, have been optimized. The charge and spin population are based on the Mulliken analysis of the electron density.36 The geometries and the normal coordinates of the species are reported in the Supporting Information (SI) in Table S1–S3.

2.2.2. Nonthermal Rate Coefficient. The VTST$^{23}$ has been adopted to calculate the rate coefficient of the present reaction, following a nonthermal (NT) approach, which resembles the experimental conditions where the ionized CO$_2^+$ is not in thermal equilibrium with the H$_2$ neutral molecule and the energy flow within the reactive complex does not follow a statistical distribution. Hence, the rate coefficient has been obtained by averaging over the translational and rotational energy, whereas the vibrational energy of CO$_2^+$ is not used in Boltzmann thermalization because its vibrational population is controlled by the amount of energy adsorbed during the photoionization process. The microcanonical nonthermal rate coefficient ($k_{NT}^{fi}$) is given by

$$k_{NT}^{fi}(T, E_V) = \sigma \int_0^\infty k_0(E_T, E_V)P_{\text{rea}}(E_T, E_V, T)dE_T$$

(1)

where $k_\mu$ is the standard bimolecular microcanonical rate coefficient, $E_V$ is the vibrational energy of CO$_2^+$, $\sigma$ the rotational symmetry factor, and $E_T$ is the translational-rotational energy of the reactants (the translational energy is referred to the center of the mass frame in which the translational energy of the TS is zero). $P_{\text{rea}}$ is the distribution probability of the reactants at temperature $T$:

$$P_{\text{rea}}(E_T, E_V, T) = \rho_0(E_V, E_T)e^{-E_T/k_BT}$$

(2)

and $\rho_0$ is the density of states of the reactants. We have considered only the vibrational energy of CO$_2^+$ because the vibrational partition function of H$_2$ is unity for all temperatures of the present theoretical study ($T \leq 300$ K) due to the high vibrational frequency of H$_2$ (4381 cm$^{-1}$).

The number of states of the reactants are

$$N_{\text{rea}}^{\text{CO}_2}(E_V, E_T) = N_{T}^{\text{CO}_2}(E_T)N_{V}^{\text{CO}_2}(E_V)N_{H2}^{\text{H}_2}(E_T)$$

(3)
where \( N_{VT}^{oi} \) is considered to be equal to 1 because at \( T \leq 300 \text{ K} \), only the first vibrational level is populated due to the high vibrational frequency of \( \text{H}_2 \).

Since \( \rho(E) = \frac{dN(E)}{dE} \), the reactant density of state is:

\[
\rho^{rea}(E, E_{TR}) = N_{VT}^{CO}(E_{CO}^{0}) \cdot \rho_{CO}^{rea}(E_{TR}) \cdot N_{TR}^{rea}(E_{TR}) + N_{VT}^{CO}(E_{CO}^{0}) \cdot \rho_{H_{2}}^{rea}(E_{TR}) \cdot N_{TR}^{rea}(E_{TR})
\]

(4)

where \( \rho_{CO}^{rea}(E_{TR}) \) is the translational-rotational density of states for the reactants and is given by

\[
\rho_{CO}^{rea}(E_{TR}) = \rho_{CO}^{rea}(E_{CO}^{0}) \cdot N_{VT}^{H_{2}}(E_{TR}) + \rho_{H_{2}}^{rea}(E_{TR}) \cdot N_{VT}^{H_{2}}(E_{TR})
\]

(5)

and \( N_{VT}^{rea}(E_{TR}) = N_{VT}^{CO}(E_{CO}^{0}) \cdot N_{VT}^{H_{2}}(E_{TR}) \).

The integral at the denominator of eq 2 is

\[
\int_{0}^{\infty} \rho^{rea}(E_{VT}, E_{TR}) e^{-E_{VT}/k_{VT}} dE_{TR} = N_{VT}^{CO}(E_{CO}^{0}) \cdot \int_{0}^{\infty} \rho_{CO}^{rea}(E_{TR}) e^{-E_{TR}/k_{VT}} dE_{TR} + \rho_{VT}^{CO}(E_{CO}^{0}) \cdot \int_{0}^{\infty} \rho_{H_{2}}^{rea}(E_{TR}) e^{-E_{TR}/k_{VT}} dE_{TR}
\]

(6)

Equation 6 can be simplified by using the Laplace transform of the density and number of states:

\[
\int_{0}^{\infty} N_{VT}^{rea}(E_{TR}) e^{-E_{TR}/k_{VT}} dE_{TR} = K_{VT} Q_{VT}^{rea}(T) \cdot Q_{VT}^{rea}(T)
\]

\[
\int_{0}^{\infty} \rho_{CO}^{rea}(E_{TR}) e^{-E_{TR}/k_{VT}} dE_{TR} = K_{VT} Q_{VT}^{rea}(T) \cdot Q_{VT}^{rea}(T)
\]

\[
\int_{0}^{\infty} \rho_{H_{2}}^{rea}(E_{TR}) e^{-E_{TR}/k_{VT}} dE_{TR} = K_{VT} Q_{VT}^{rea}(T) \cdot Q_{VT}^{rea}(T)
\]

(7)

where \( Q_{VT}^{rea}(T) \) is the rotational partition function of the VTS complex relative to the set \( V_{VT} \) and \( Q_{VT}^{rea}(T) \) is the rovibrational partition function of the reactants at temperature \( T \).

The vibrational number of states is much greater than the density number of states up to \( T = 300 \text{ K} \); hence, the term \( \rho_{CO}^{rea}(E_{CO}^{0}) \cdot K_{VT} \) in eq 7 can be neglected.

Equation 2 then can be rewritten as follows:

\[
P^{rea}(E_{TR}, E_{VT}^{CO}, T) = \frac{\rho^{rea}(E_{VT}, E_{TR}) e^{-E_{VT}/k_{VT}}}{Q_{VT}^{rea}(T) \cdot Q_{VT}^{rea}(T) \cdot N_{VT}^{CO}(E_{CO})}
\]

(8)

where \( E_{TR} = E_{VT}^{CO} + E_{VT}^{H_{2}} \).

The microcanonical rate coefficient can be written as

\[
k_{\mu}(E, E_{VT}) = \frac{\sigma N_{VT}^{TS}(E_{VT}, E_{VT}^{TS})}{h \rho^{rea}(E_{VT}, E_{TR})}
\]

(9)

where the number of states of the transition state (\( N_{VT}^{TS} \)) in the reference frame of the center of mass of the reactants, depends on the vibrational (\( N_{VT}^{TS} \)) and rotational (\( N_{VT}^{TS} \)) number of states:

\[
N_{VT}^{TS}(E_{VT}, E_{VT}^{TS}) = N_{VT}^{TS}(E_{VT}^{TS}) \cdot N_{VT}^{TS}(E_{VT})
\]

(10)

By substituting the eqs 8 and 9 into eq 1, the translational-rotational averaged nonthermal rate coefficient can be rewritten as:

\[
k_{\mu}^{NT}(T, E_{VT}) = \frac{\sigma}{h} \int_{0}^{\infty} N_{VT}^{TS}(E_{VT}, E_{VT}^{TS}) \cdot N_{VT}^{TS}(E_{VT}) e^{-E_{VT}/k_{VT}} dE_{TR}
\]

(11)

and because \( \int_{0}^{\infty} N_{VT}^{TS}(E_{VT}) e^{-E_{VT}/k_{VT}} dE_{TR} = K_{VT} Q_{VT}^{TS}(T) \), eq 11 became

\[
k_{\mu}^{NT}(T, E_{VT}) = \frac{\sigma N_{VT}^{TS}(E_{VT}) [K_{VT} Q_{VT}^{TS}(T)]}{h Q_{VT}^{rea}(T) Q_{VT}^{rea}(T) N_{VT}^{CO}(E_{CO})}
\]

(12)

We consider TS as divided into two vibrational subsystems \((a\) and \(b)\) not interacting with each other. System \( a \) is referred to the frequencies associated with the \( \text{CO}^{+} \) modes not thermalized, and \( b \) to the intermolecular vibrations thermally averaged. Then, the vibrational number of states of TS can be written as

\[
\langle N_{VT}^{TS}(E_{VT}) \rangle_{VT} = \frac{N_{VT}^{TS}(E_{VT})}{h Q_{VT}^{rea}(T) Q_{VT}^{rea}(T) N_{VT}^{CO}(E_{CO})}
\]

(13)

that gives the nonthermal rate coefficient:

\[
k_{\mu}^{NT}(T, E_{VT}) = \frac{\sigma K_{VT} Q_{VT}^{TS}(T) Q_{VT}^{TS}(T) N_{VT}^{TS}(E_{VT})}{h Q_{VT}^{rea}(T) Q_{VT}^{rea}(T) N_{VT}^{CO}(E_{CO})}
\]

(14)

where \( Q_{VT}^{TS}(T) \) is the rotational partition function for the VTS complex, \( Q_{VT}^{rea}(T) \) is the relative translation molecular partition function of the reagents, \( Q_{VT}^{rea}(T) \) is the rovibrational partition function of \( \text{H}_2 \), \( Q_{VT}^{rea}(T) \) is the rotational partition function of \( \text{CO}^{+} \), and \( N_{VT}^{CO} \) is the number of vibrational states of \( \text{CO}^{+} \). \( Q_{VT}^{TS}(T) \) is the vibrational partition function of the VTS complex relative to the set \( V_{VT} \), \( N_{VT}^{TS} \) is the number of vibrational states of the VTS complex relative to the set \( V_{VT} \). The number of vibrational states have been calculated by direct count (Beyer-Swinehart algorithm).

Moreover, to calculate the rate coefficient of the reaction, it is relevant to know the energy, named \( E_{TS} \), acquired by the reactive complex when moving along the barrierless minimum energy path (MEP) from reagents to the VTS geometry. \( E_{TS} \) can be distributed among the internal degrees of freedom of the VTS complex as well as in the relative kinetic energy of the two products. The dynamics that control such energy "flow" are subtle and depend on several factors, such as the internal energy content of the reagents and the timescales of the internal vibration rearrangement (IVR) within the VTS complex. In thermal equilibrium conditions, the canonical rate coefficient is

\[
k_{can}(T) = \frac{\sigma}{h Q_{rea}(T)} \int_{0}^{\infty} N_{VT}^{TS}(E + X(T)) e^{-E/k_{VT}} dE
\]

(15)
the reaction energy flow toward the internal degrees of freedom of the reaction complex, vice versa, when $X(T)$ goes to zero, all the reaction energy remains in the reaction coordinate and eventually goes into the relative kinetic energy of the products. Equation 15 can be solved to give the standard canonical form of the rate coefficient with an exponential part depending on the $X(T)$:

$$
\sigma = \frac{kT}{h} Q_{\text{rea}}(T) e^{X(T)/kT}
$$

In the nonthermal condition of the present experiments, eq 16 cannot be applied, while eq 14 should be used after accounting properly the effect of $X(T)$ within the VTS complex.

The nonthermal rate coefficient (eq 14) is transformed as follows:

$$
I_{\text{NT}}(T, E) = \frac{\sigma Q_{\text{trans}}(T) Q_{\text{vib}}(T) N^{\text{Vib}}(E + X) X(T) - E(T) e^{X(T)/kT}}{h Q_{\text{rea}}(T) Q_{\text{vib}}(T) N^{\text{Vib}}(E)}
$$

where $X(T) - E(T)$ is the energy flow going into the intermolecular vibrations ($V_i$) of the VTS complex, whereas the $X(T) - E(T)$ is the energy flow going into the vibrations ($V_j$) of the VTS complex associated with $CO_2$. The sum of $X_i$ and $X_j$ is always equal to 1.

3. RESULTS AND DISCUSSION

In the explored photon energy range from 13.7 to 15.0 eV, the carbon dioxide is ionized (ionization energy = 13.777 ± 0.001 eV) and vibrationally excited in its ionic ground state $X^2\Pi_{3/2,1/2}g$ without dissociation, as several spectroscopic studies of $CO_2^+$ have demonstrated. The mass spectrum of $CO_2$ measured at 14.0 eV photon energy in the range $10 < m/z < 48$ is shown in Figure 1a, where neither fragment ions nor water traces are observed. The introduction of the $H_2$ molecule in the reaction cell at a pressure of $9.0 \times 10^{-5}$ mbar induces the hydrogen atom transfer (HAT) reaction 18 that generates the protonated form of carbon dioxide (inset in Figure 1a) $HCO_2^+$ detected at $m/z = 45$.

$$
CO_2^+ + H_2 \rightarrow HCO_2^+ + H
$$

To evaluate the isotopic effect, the reaction was also performed with $D_2$ and, as expected, a peak at $m/z = 46$ due to the $CO_2D^+$ ion was recorded. In Figure 1b, the spectra obtained at the photon energy 14.0 eV with $H_2$ ($D_2$) in the reaction cell at the nominal pressure of $3.0 \times 10^{-5}$ mbar are shown. By fitting the area of the peaks at $m/z = 44, 45$ and 46, the obtained ratios $CO_2^+/HCO_2^+ = 1.3$ and $CO_2^+/DCO_2^+ = 2.12$ give an isotopic effect of 1.6.

The reactions were also studied at fixed photon energy ($h\nu = 14$ eV) to verify the linear increase of the $H(D)CO_2^+/$$CO_2^+$ ratio with the pressure of $H_2(D_2)$ in the reaction cell (Figure 2a) and by scanning the photon energy from 13.7 to 15.0 eV to...
measure the H(D)CO$_2^+$/CO$_2$ ratio as a function of photon energy at a fixed H$_2$(D$_2$) pressure (Figure 2b). The experimental data in Figure 2b show that the reaction is not favored by the increase of the vibrational energy of the CO$_2^-$. Literature data at room temperature (298 K) and at low pressure report rate coefficients $k$ of $5.80 \times 10^{-10} \pm 10\%$ and $4.10 \times 10^{-10} \pm 10\%$ molecule$^{-1}$ s$^{-1}$ cm$^2$ for the reaction with H$_2$ and D$_2$ respectively, whereas the rate coefficients reported by Gerlich and co-workers at high pressure are $9.5 \times 10^{-10} \pm 20\%$ and $4.9 \times 10^{-10} \pm 20\%$ molecule$^{-1}$ s$^{-1}$ cm$^2$ for reaction with H$_2$ and D$_2$, respectively. Consequently the calculated isotopic effect ($k_{H_2}/k_{D_2}$) at low pressure is $1.4 \pm 0.3$ which is in quite good agreement with our low pressure experimental result of 1.6 obtained from data shown in Figure 1b. Moreover, the Langevin rate coefficients at high pressure are $5.80 \times 10^{-10} \pm 20\%$ and $4.10 \times 10^{-10} \pm 20\%$ molecule$^{-1}$ s$^{-1}$ cm$^2$ for the reaction with H$_2$ and D$_2$, respectively, demonstrate that the reaction efficiency relative to collision rate, $(k_{H_2}(H_2))/k_L$, is about 38% at low pressure and it is 62% $(k_{H_2}(H_2))/k_L$ and 45% $(k_{D_2}(D_2))/k_L$ when Gerlich’s data are considered.$^{23}$

The mechanism of this reaction is unveiled by the theoretical calculations performed at the DFT level of theory to compute the MEP, and by VTST to calculate the rate coefficients. All energies reported hereafter are corrected for zero point energy (ZPE).

The MEP reported in Figure 3 shows that reaction 18 is barrierless, with a minimum (blue arrow) at $-134$ kJ/mol

![Figure 3. Minimum Energy Path of the reaction between CO$_2^+$ and H$_2$ molecule. The zero energy is referred to the entrance channel of the reactants. The red arrow points to the geometry of the VTS Complex, whereas the blue arrow points to the minimum (MIN) of the MEP. The level of calculation is B2PLYP/6-31++G** with ZPE correction.](image)

($-142$ kJ/mol for D$_2$) that has a dissociation energy of $12.1$ kJ/mol ($13.3$ kJ/mol for D$_2$) to form the products HCO$_2^+ + H$.

The reactive complex at MIN of the MEP has the two hydrogen atoms separated by $1.55$ Å, while the interatomic distance between O and H is $1.02$ Å. This structure shows that the reaction has almost already occurred with the atomic hydrogen weakly bound to the ionic product HCO$_2^+$, which remains quasi-linear, as well as the O–H–H group. From a dynamical perspective, the reaction proceeds with the H–H approaching one of the oxygen lone pair while the outgoing H atom bounces back along the direction over which the H–H has entered the reaction region. The geometry of the transition state is calculated by variational minimization of the number of vibrational states of the reactive complex along the reactive coordinate. In Figure 3, the position of VTS is indicated by a red arrow, and its energy is about $16$ kJ/mol ($19$ kJ/mol for D$_2$) higher than MIN, about $4$ kJ/mol ($5$ kJ/mol for D$_2$) above the energy of the products. In this VTS, the H–H bond is partially broken ($1.12$ Å), and the O–H bond is quasi-formed ($1.22$ Å).

The electronic nature of the VTS can be analyzed in terms of the partial charges $q$ (see Figure 4a), where the outgoing hydrogen atom ($\text{SH}$) has a $q$ of $0.3e$, while the $q$ value of CO$_2$ is $0.47e$, which is almost the value ($0.5e$) it reaches in the final products.

It is noteworthy that the positions along the MEP of the minimum of the $q$ of CO$_2$, as well as of the maximum of the $q$ of the outgoing H, are very close in the VTS: the partially positive charged outgoing hydrogen ($\text{SH}$) has to be filled with half an electron charge to became neutral and to reach the final product region. The partial spins of the reactive systems are also interesting especially when considering the hydrogen atom which is transferred from H$_2$ to CO$_2$: in the reactant region as well as in the final product region, this hydrogen has a zero net value of its partial spin; meanwhile, a maximum value of about $0.2\hbar$ is reached in the neighborhood of the VTS.

From a dynamical point of view, the maximum of the partial charge of the outgoing hydrogen and the corresponding maximum of the partial spin of the “transferred” hydrogen are correlated to a slowing down of the speed of the reaction: in this region of the MEP, where the VTS is located, the system decelerates its way toward the products. The break of the strongly bound H$_2$ molecule is the key factor in the determination of the rate coefficient and the electron density of both H atoms is strongly shaken up during the reaction.

As for the energetics of the reaction, the low-pressure experimental conditions of the present study are such that the CO$_2^+$ and the VTS complex are not in thermal equilibrium in their internal degrees of freedom as well as with the surrounding molecules. The hydrogen molecule is at room temperature, as well as the roto-translation degrees of freedom of the CO$_2^+$ ion. Instead, the CO$_2^+$ vibrational states are excited by the energy absorbed during the photoionization and hence, not in thermal equilibrium with the surrounding. Furthermore, the H$_2$ molecule plays a peculiar role with its high vibrational energy ($4381$ cm$^{-1}$), which is poorly coupled with the other lower energy vibrations of the VTS complex, leading to a nonthermalized system. Hence, the vibrations of the transition state (see Table S4 in the Supporting Information) have been classified according to the following scheme: four frequencies form the set ($\nu_V$) associated with the CO$_2$ ion ($578, 608, 1283, 2386$ and $578, 585, 1270, 2383$ cm$^{-1}$ in the reaction with H$_2$ and D$_2$, respectively), the negative frequency at $-245$ cm$^{-1}$ for H$_2$ ($-181$ cm$^{-1}$ for D$_2$) is associated with the reactive coordinate, and the other four vibrations ($311, 909, 1068, 1170$ and $232, 650, 776, 882$ cm$^{-1}$ in the reaction with H$_2$ and D$_2$, respectively) are classified as the set ($\nu_N$ of intermolecular modes. These last frequencies are not considered when computing the number (N) of vibrational states of the VTS complex, which depends only on the frequencies associated with the CO$_2^+$ ion excited in photoionization, whereas the intermolecular vibrational modes of the VTS are considered to compute the corresponding vibrational molecular partition function (see eqs 13 and 14). $E_{TS}$ is the difference between the energy of VTS ($E_{VTS}$) and reagents ($E_{rea}$) and its values are $-118.2$ and $-124.0$ kJ/mol.
for H$_2$ (Figure 3) and D$_2$, respectively. In order to obtain the fraction $X$ of $E_{TS}$ (see eq 16), which goes into the VTS complex, we used the experimental reaction rates obtained by Gerlich and co-workers in the temperature range between 15 and 300 K for reaction 18. By equating eq 16 with the $k(T)$ obtained by Gerlich and co-workers, the fraction $X(T)$ as a function of $T$ can be derived, and it is shown in Figure 5.

Figure 5. Energy flow fraction $X(T)$ versus temperature. A fraction $X$ of the energy $E_{TS}(Xe_{TS})$ is transferred to the vibrational degrees of freedom of the TS. In blue is reported the energy fraction obtained by using the experimental rate coefficients for H$_2$ measured by Gerlich and co-workers. The brown area shows the uncertainty due to the 20% error on the experimental rate coefficients. The cyan line represents similar data for reaction with D$_2$.

$X(T)$ at 15 K is $4.5 \times 10^{-4}$ and $14.5 \times 10^{-4}$ for H$_2$ and D$_2$, respectively, showing that at low temperature, the $E_{TS}$ remains along the reaction coordinate and goes to the relative kinetic energy of the products. $X(T)$ slowly increases with temperature, up to $6.1 \times 10^{-2}$ and $6.6 \times 10^{-2}$ for H$_2$ and D$_2$, respectively, at room temperature. The $X(T)$ obtained in the temperature range 15–300 K has been fitted with the function $X(T)$ whose parameters are reported in Table 1.

Hence, we have calculated the nonthermal rate coefficients (eq 17) at different energies for several values of the $X_eX_b$ pair" at room temperature (300 K) when $X(300 K) = 0.0612$. Figure 6 reports such calculations for H$_2$ (Similar data for the reaction with D$_2$ are reported in Figure S2 of the Supporting Information) when $X_e$ is 0.1 and $X_b$ 0.9.

Figure 6. Rate coefficients as a function of the internal energy of CO$_2^+$ when vibrational energy distributions inside the VTS has a "$X_eX_b$ pair" equal to 0.1 and 0.9. The data are referred to $X(300 K) = 0.0612$. In the inset are reported the rate coefficients for different values of the internal energy of CO$_2^+$ and as a function of $X_e$. See further details in the main text.

Rate coefficients presented in Figure 6 show that the reaction slows down when the internal energy increases and that below 1.0 eV the rate coefficients oscillate because of a competition between the population of the vibrational levels of CO$_2^+$ and that of the VTS complex. The increase in the population of the vibrations of the VTS complex produces an increase in the rate coefficient, while the increase in the population of the vibrations of the CO$_2^+$ induces a decrease in the rate coefficients. The rate coefficient is higher when the energy flow goes to the intermolecular vibrations ($V_b$) of the VTS complex without exciting the vibrations of the VTS complex associated with CO$_2^+$ normal modes ($V_a$) (see the low values of $X_e$ in the inset of Figure 6). The rate coefficient decreases up to below $10^{-10}$ cm$^3$ s$^{-1}$ molecule$^{-1}$ when the energy flow does not go to the intermolecular vibrations ($V_b$) of the VTS complex (see the high values of $X_e$ in the inset of Figure 6). This trend can be rationalized considering how the vibrations that mainly favor the reaction are those associated with the formation of the O–H bond, and hence, all the four

|         | $\alpha$ | $\beta$  | $\gamma$ | $\delta$   |
|---------|----------|----------|----------|------------|
| H$_2$   | 1.7667   | 22.4123  | 0.3320   | 3.3205 $\times 10^{-4}$ |
| D$_2$   | 1.5483   | 19.4790  | 0.3176   | 1.2225 $\times 10^{-4}$ |
intermolecular vibrations ($V_6$) of the VTS complex. Vice versa when the energy flow goes to the four vibrations ($V_{ii}$) of the VTS complex that come from CO$_2$`, then the reaction is not favored because these vibrations are not relevant for the hydrogen transfer from H$_2$ to CO$_2$. From a theoretical point of view, it is not so simple to provide a quantitative scenario describing the real energy flow between the two vibrational subsystem $V_a$ and $V_6$ of the VTS complex even if it could be expected that low values of $X_a$ and complementary high values of $X_6$ should correspond to the real dynamical description of the reaction. In order to verify such hypothesis, we have transformed the HCO$_2$`/CO$_2$` ratio vs photon-energy data of Figure 2b in rate coefficients vs internal energy, following the procedure described in the paragraph 3 of the Supporting Information. The average internal energy of the CO$_2$` ion as a function of photon energy (Figure S1) allows to plot the experimental rate coefficients as a function of the internal energy of the CO$_2$` ion, and hence to compare the theoretical and experimental rate coefficients (see Figure 7a for H$_2$ and Figure S3 for D$_2$).

It is noteworthy that the “$X_a$,$X_6$ pair” is a relevant parameter to select a theoretical rate coefficient in agreement with the experimental data. The $X_a(X_6) = 0.1(0.9)$ is the best pair of parameters which is able to correctly reproduce the reaction kinetic at $T = 300$ K for reaction with H$_2$ whereas the $X_a(X_6) = 0.0(1.0)$ seems to better reproduce the reaction with D$_2$ (see Figure S3 of the Supporting Information). In terms of energy flow, this means that for the reaction with H$_2$ ($E_{TS} = -118.2$ kJ/mol), only $X_aX(300 K)$--$E_{TS} = 0.7$ kJ/mol is the energy that flows into the “CO$_2$`-like” vibrational levels ($V_a$) of the VTS complex, while $X_6X(300 K)$--$E_{TS} = 6.5$ kJ/mol is the energy that goes to the intermolecular vibrations ($V_6$) of the VTS complex. For the reaction with D$_2$ ($E_{TS} = -124.0$ kJ/mol), all the energy goes to the intermolecular modes of the VTS, and $X_6X(300 K)$--$E_{TS} = 8.1$ kJ/mol. Hence, the relative kinetic energy of the two products H and HCO$_2$` is 111.0 kJ/mol, while for D and DCO$_2$`$^+$ it is 115.9 kJ/mol. This means that the reaction occurs so quickly that there is no much time to share the reaction energy with the internal degrees of freedom of the VTS complex.

Because of the small amount of energy $X(T)$--$E_{TS}$ transferred to the VTS complex at $T = 300$ K, which will be even smaller at lower $T$ (see Figure 5), it is reasonable to assume that the “$X_a$,$X_6$ pair” is independent from the temperature itself. Hence, in the temperature range between 15 and 300 K, where the $X(T)$ is known, the rate coefficients can be calculated (see Figure 7b for H$_2$ and Figure S4 for D$_2$). The rate coefficients increase when the $T$ decreases (see Figure S5 of the Supporting Information), and at $T = 15$ K, the reaction accelerates up to about $1.5 \times 10^{-9}$ molecule$^{-1}$ s$^{-1}$ cm$^3$ for H$_2$ reaction (the collision limit), keeping the decreasing oscillating trend with energy at every $T$ between 15 and 300 K (see Figure 7b). The general decreasing trend of the rate coefficient with the increase in the vibrational energy of CO$_2$` has the same decreasing behaviors of the Gerlich’s rates with temperature, where only the populations of the translational and rotational levels are involved. Hence, this reaction is not favored when either vibrational or roto-translational energy content are increased as generally expected in the barrierless reactions.

For reaction with D$_2$, the temperature trend of the rate coefficient (see Figure S6 of the Supporting Information) has a maximum at about 55 K for all the energies up to 2 eV, and $k = 6.5 \times 10^{-10}$ molecule$^{-1}$ s$^{-1}$ cm$^3$ is reached for $E = 0$ eV. The reason for the different temperature trend of the rate coefficients for H$_2$ and D$_2$ is the different fraction $X(T)$: for both reactions, $X(T)$ decreases with the temperature, but in the reaction with D$_2$, the energy flow fraction at low $T$ is greater than the one for the reaction with H$_2$ (see Figure S5). Hence, the exponential part of eq 17 ($e^{X_aX(T)}$--$E_{TS}$/$kT$), which makes the rate coefficient decreasing with decreasing $T$, is more effective in decreasing the rate coefficient below 55 K for the reaction with D$_2$, then in the case of the reaction with H$_2$. The rate coefficients for D$_2$ at low temperatures have a different behavior in the present work with respect to thermal Gerlich’s data, and this can be explained with the nonstatistical energy distribution in the experimental conditions in our work.

4. CONCLUSIONS

The reaction of CO$_2$` with hydrogen molecules has been studied as a function of the CO$_2$` internal energy by using tunable synchrotron radiation to perform photoionization
mass-resolved experiments, which have been analyzed and rationalized by means of the energetic and kinetics theoretical model. The reaction proceeds via hydrogen transfer from H₂ to CO₂⁺ with HCO₂⁻ and H as final products. The experimental ratio of the charged product over the charged reactant shows a decrease in the reaction rate with increasing photon energy, confirmed also by the reaction of CO₂⁺ with D₂. The DFT minimum energy path of the reaction is barrierless and exothermic, and the variational transition state is located near the minimum of the energy along the reaction coordinate. Charge and spin population analysis clearly marks a strong reshuffle of the electron density when the reactive complex reaches the VTS geometry. The rate coefficient has been evaluated taking into account the nonthermal experimental conditions because of the low pressures in the reaction chamber. Moreover, the kinetic calculations considered the decoupling of the high energy vibration of H₂ with respect to the lower energy vibrations of CO₂⁺, and this is reflected in two vibrational sets of the VTS complex, which give different contribution to the overall reaction rate. The energy produced along the reaction coordinate is parameterized in terms of flows toward either the relative kinetic energy of the products or the internal degrees of freedom of the reactive complex. The present theoretical model gives an interpretation of the experimental data in terms of energy flow, revealing a decreasing trend of the rate coefficients with the photoionization energy. Furthermore, calculations of the reaction rates at different temperatures of the reactants confirm that the reaction at lower temperature reaches almost its Langevin upper limit of 1.53 × 10⁻⁹ molecule⁻¹ s⁻¹ cm⁻³. This study provides kinetic information that deserves to be considered within the network of the chemical reactions occurring where CO₂ and H₂ are present.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.2c01695.

Data reported: normal coordinates at the B2PLYP/6-31+ +G** level of theory for reactive complex in its VTS geometry in the reaction of CO₂⁺ with both H₂ and D₂; cartesian coordinates of reagents, products and VTS; normal mode analysis of the vibrational frequencies of the VTS geometry; average internal energy distribution upon photoionization; rate coefficients for the reaction of CO₂⁺ with H₂ and D₂ in a range of Xe◦ pair; rate coefficients versus temperature of the reactants (PDF)

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