Three-body kinematical correlation in the dissociative recombination of CH$_2^+$ by three-dimensional imaging


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A three-dimensional imaging technique installed at the Heidelberg Test Storage Ring (TSR) has been used to investigate the three-body breakup channels occurring in the dissociative recombination process of the methylene ion CH$_2^+$. By selecting dissociation planes perpendicular to the molecular beam direction the dissociation kinematics could be measured with unprecedented momentum resolution. Release energies, the relative branching ratio, and the kinematical correlations between the three fragments were determined for the two energetically allowed channels: C(3P) + H(2S) + H(2S) and C(1D) + H(2S) + H(2S).

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I. INTRODUCTION

In dilute plasmas which are cold enough to contain molecular ions, dissociative recombination (DR) is the dominant process for removing electrons. The process is thereby not only controlling the amount of ionization in these media, it also constitutes an important loss channel for molecular ions and a source of energetic neutral atoms and excited molecules. DR rates, branching ratios, and the energy sharing between inner and outer degrees of freedom of the fragments are thus important ingredients in modeling these plasmas.

Even though the basic principle of DR has been known for more than 50 years [1] and a close to quantitative understanding of the DR of diatomic molecular ions has been achieved in the meantime [2], the theoretical description of the DR process of polyatomic ions is still in its infancy; only recently theory succeeded in reproducing the measured DR rate for the simplest three-atom system H$_3^+$ [3], one of the main difficulties being caused by the two-dimensionality of the process. On the experimental side, considerable progress has been made since the advent of heavy-ion storage rings with merged electron beams, which do allow one to control the inner excitation of the molecular ions and the relative ion-electron energy precisely enough to produce data in the parameter space of interest for, e.g., planetary atmospheres or interstellar chemistry [4], and accessible to theoretical considerations. Despite these experimental advances, in particular in the study of diatomic systems, detailed investigations of the DR process for polyatomic ions, such as measurements of branching ratios at relative energies other than zero, of the inner excitation of neutral molecular fragments, of angular distributions, or of the dissociation kinematics are still limited by the presently available detection techniques for DR reaction products.

Recently, we have installed a three-dimensional (3D) imaging system at the Heidelberg Test Storage Ring (TSR) [5], which is based on the concept of Strasser et al. [6] and allows one to measure all three velocity components of the DR fragments and thus provides experimental access to study the dissociation kinematics of polyatomic molecular ions. In dissociative recombination the released energy is transferred to translational degrees of freedom of the products and to their internal excitation. For diatomic molecules, the way in which the energy is shared between the two fragments is fixed by energy and momentum conservation. For DR reactions of polyatomic molecules that yield three or more fragments, however, the energy and momenta restrictions alone do not determine uniquely the dissociation kinematics, but the final magnitudes and relative directions of the fragments momenta are influenced by the dissociation dynamics as well. Previously, the dissociation kinematics of the DR products of the triatomic molecular ion, H$_3^+$, and its isotopomers, D$_3^+$, H$_2$D$^+$, and D$_3$H$^+$, at zero relative ion-electron energies could be studied at the TSR by 2D imaging of the two- and three-body dissociation channels [7], i.e., by measuring only transversal velocities of the fragments. In these specific cases, the presence of only one dissociation channel with three fragments, sharing a single fixed kinetic energy release, permitted us to extract the dissociation kinematics by 2D imaging alone. In general, however, the use of 2D imaging for inferring the dissociation geometries of three-body and higher multiplicity DR reactions is severely restricted if not impossible; the measurement of all three velocity components of the fragments is required to be able to access this information.

In the present paper, we report on our first measurement of the three-body breakup of a triatomic molecular ion using the new 3D imaging system. Even though the time resolution of the system and thus the resolution for the longitudinal fragment velocities was not yet optimal at the time of the experiment, we could separate the different three fragment channels and determine uniquely their kinematical properties as well as their relative branching ratios. The study was performed for the methylene cation CH$_2^+$, where the DR at zero relative electron-ion energy leads to two three-fragment channels:

$$\text{CH}_2^+(\tilde{X}^2A_1) + e^- \rightarrow C(3P) + H(2S) + H(2S) \rightarrow C(1D) + H(2S) + H(2S).$$

Several reasons prompted us to choose the CH$_2^+$ ion for this
II. EXPERIMENTAL PROCEDURE

A. Experimental setup

The experiments presented here were carried out at the Test Storage Ring (TSR) of the Max-Planck-Institut für Kernphysik in Heidelberg, Germany. A beam of 6.68 MeV CH$_2^+$ ions was formed in the stripper gas channel located in the terminal of a tandem Van de Graaf accelerator by fragmentation of a primary 4.7 MeV CH$_3$O$^-$ ion beam, which was produced by a sputter source. The ions were injected into the storage ring and kept circulating for up to 11 s at a residual background gas pressure of 3 x 10^{-11} mbar.

During storage, the ions were continuously subjected to the influence of an electron beam produced by the thermal cathode of the TSR electron target [11]. The electrons were copropagating with the ions over an effective distance of ~1.25 m at zero average relative velocity. Thereby the ion beam was phase-space cooled within ~2 s and kept cold during the course of the subsequent DR measurements. The transversal and longitudinal temperature of the electrons was $kT_\perp = 3.7$ meV and $kT_\parallel = 58$ $\mu$eV, respectively, while the electron density was chosen to be between $6 \times 10^6$ cm$^{-3}$ and $2 \times 10^7$ cm$^{-3}$. For some runs the electron cooler, located in a different quadrant of the TSR, was used in addition to speed up phase-space cooling. Depending on the actual cooling times reached only events recorded after a storage time of >2–3 s have been considered in the final data analysis. As shown in Coulomb explosion imaging measurements on CH$_2^+$ [12], this time cut also ensures that all molecules have quantitatively relaxed to the vibrational ground state, while remaining excitations of the ground state rotational bands are expected to reach full equilibrium with the 300 K background radiation only at the end of the measuring cycle.

Neutral fragments of the molecular CH$_2^+$ ion that underwent a DR process in the interaction region of the electron target (energy in the ion-electron center of mass system $E_{c.m.} = 0 \pm 3.7$ meV) were detected downstream of the electron target by the new 3D fragment-imaging setup located at a distance of 12.24 m from the center of the interaction region. The 3D detector consists of a 80 mm diameter Chevron microchannel plate (MCP) coupled to a fast phosphor screen [P-47 (Y$_2$SiO$_5$:Ce), decay time $\tau = 54$ ns], which is faced by two charge-coupled device (CCD) cameras, one of which is equipped with a fast optical shutter. For a detailed description of this new 3D imaging technique the reader is referred to Refs. [5,6]. Briefly, the lateral impact positions of the DR fragments on the MCP plane are derived as usual from the position of the light spots observed by the nongated CCD camera, which is integrating the fluorescence light emitted from each spot over a long time compared to the characteristic decay time $\tau$ of the phosphor screen. In contrast, the light integration of the gated CCD camera is stopped after a fixed gating time $t_g$, which is started by the fragment arriving first at the MCP. Thus, in case $t_g$ is short compared to $\tau$, the spot intensity measured by the gated CCD camera, normalized to the total spot intensity as determined by the nongated camera, is a measure of the impact time difference of the fragment with respect to the fastest one. As the velocity of the center of mass is known (in the present experiment the beam velocity), the setup thus allows us to determine all three velocity components of the fragments.

The two CCD cameras were synchronized and read out at a frame rate of 30 Hz. As the number of events recorded by the MCP were of the order of 1 kHz, the phosphor screen was operated in a trigger mode, switching off the acceleration voltage between the MCP and the screen within ~5 $\mu$s after an event was seen by the MCP. In this way, the probability of observing two independent events within one frame could be kept in the range of a few percent.

B. Data analysis

The data was first sorted according to the number of distinguishable light spots recorded simultaneously in both the gated and ungated CCD camera using a peak finding routine. The minimum distance between two spots was ~5 mm. The transversal $(x_\perp, y_\perp)$ coordinates of each fragment were then deduced from the light spots observed by the nongated CCD camera with an accuracy of ~150 $\mu$m. The pixel-to-mm conversion was determined by means of a metal plate with a set of holes 10 mm apart, which was placed during one measurement in front of the MCP, the accuracy of the conversion factors being $\pm 1\%$. The mass assignment of the three fragments following the DR of CH$_2^+$ was performed in the usual way by calculating the (transversal) center of mass (c.m.) of the event for all three possible permutations and selecting the mass assignment resulting in a c.m. being closest to the beam center. In a second step, the transversal coordinates of the three fragments with respect to the c.m. of the event are derived, restricting the further analysis to frames with c.m. within a distance $R_{c.m.} \leq \sigma_R$ from the beam center, $\sigma_R$ being the variance of the c.m. distribution around the beam center. Finally, the total projected distance $D$ is calculated by
by the finite efficiency of the MCP and by fragments from breakup reactions of the circulating molecules on the TSR rest gas. As for these frames the electronic gate is started by the fragment itself, \( t_g = 0 \), and Eq. (3) results in

\[
\tau = -\ln\left(\frac{1 - \frac{\tilde{\Omega}_i}{k}}{1 - \frac{\tilde{\Omega}_j}{k}}\right).
\]

A typical \( t_g \) distribution obtained in this way is shown in Fig. 1(b).

While the observed variation in the position can be readily explained to be caused by various experimental imperfections of the CCD cameras and of the image intensifier used as an optical shutter, the discussion of the origin of the position dependence of \( t_g \) is more intricate. The \((x,y)\)-dependence of \( t_g \), which amounts to 1.5 ns when comparing the central area of the detector, mainly hit by carbon fragments, to the outer areas hit by the hydrogen atoms, can be due to at least three causes: A position (intensity, rate) dependence of (i) the electronic trigger derived from the MCP, (ii) the actual closing time of the shutter, and (iii) the decay time of the phosphor screen. As we are finally only interested in the impact time difference, which is independent of the time the electronic trigger has been started, effects due to (i), while influencing the single particle frame analysis, would drop out in the analysis of the DR measurements. By performing the DR analysis assuming (a) the total variation being due to (i), and (b) the effects being solely due to (ii) and (iii), it turns out that only procedure (b) results in symmetric distributions of the impact time differences. The impact time difference between two of the fragments was therefore deduced by

\[
\Delta t_{i,j} = t_i - t_j = \tau \ln\left(\frac{1 - \frac{\tilde{\Omega}_i}{k}}{1 - \frac{\tilde{\Omega}_j}{k}}\right) + t_g(i) - t_g(j),
\]

properly smoothing the measured \( k(x,y) \) and \( t_g(x,y) \) distributions to avoid statistical artifacts.

The \( \Delta t_{i,j} \) distribution resulting from the DR of \( \text{CH}_2^+ \) into the three-fragments channels is shown in Fig. 2, each event contributing two entries to the histogram. For symmetry reasons the graph is required to be reflection symmetric around \( \Delta t_{i,j}=0 \), which is indeed fulfilled if the \( t_g \) correction is applied as discussed above. Also shown is the result of a Monte Carlo simulation assuming the time resolution for the individual impact times \( t_i \) to be \( \sigma_t = 0.9 \) ns. Comparing \( \sigma_t \), the maximum time-of-flight difference of \( \sim 6 \) ns, it is obvious that the time resolution achieved is not yet sufficient to allow for a detailed three-dimensional analysis of the dissociation kinematics of \( \text{CH}_2^+ \). To reach an optimal time resolution the gating time should be only slightly larger than the maximum time-of-flight difference of the fragments. At the time of the present experiment, however, the shortest gating time that could be realized was \( t_g \sim 20 \) ns [compare Fig. 1(b)], which was mainly determined by the transient time of the trigger pulse through the electronics. We are presently implementing a delay line for the light seen by the gated camera [5], which will allow us to optimize the integration time with respect to the flight time differences in future experiments.
In view of the limited time resolution reached in the present experiment, the time information was only used in the following analysis to select DR events where the normal of the molecular plane was oriented parallel to the beam direction. For this purpose the angle $\theta$ between the beam axis and the normal of the molecular plane was calculated event by event from the measured c.m. velocities of the three fragments. A histogram of the number of DR events as a function of the c.m. direction. For this purpose the angle $\theta$ of the molecular plane was oriented parallel to the beam direction. The measured time distribution was adjusted to the height of the measured distribution around $|\Delta t_{HC}|=0$ ns. The simulated curve was adjusted to the height of the measured distribution around $|\Delta t_{HC}|=0$ ns.

C. Monte Carlo simulations

All analysis steps are accompanied by detailed Monte Carlo (MC) simulations that mimic the dissociation process. The simulations include the following assumptions and steps: (i) The dissociation planes are isotropically oriented, and the individual momenta of the fragments—if not otherwise stated—are randomly distributed in the Dalitz circle (see Sec. III A). (ii) The kinetic energy release $E_k$ for the $C(1^3P)$ channel with respect to the rovibrational ground state of CH$_2^+$ is fixed to that of the $C(3^3P)$ channel by $E_k(1^1D)=E_k(3^1P)-1.264$ eV [13]. Moreover, if not varied, $E_k(3^3P)$ and the $[C(3^3P)]/[C(1^1D)]$ branching ratio are taken to be 2.62 eV and 68.32, respectively. (iii) A rotational excitation of the ground vibronic state [14] is assumed according to a Maxwell-Boltzmann distribution for a temperature of 300 K. (iv) The dissociation occurs randomly and uniformly in the interaction region (effective length 1.25 m; mean distance to the imaging detector $s_0=12.24$ m). (v) The dissociation events are generated having molecular c.m., which are normally distributed around the beam center with a standard deviation that typifies the measured c.m. distribution. Moreover, the time-of-flight of each fragment is chosen to be normally distributed with a standard deviation $\sigma_t$. The simulated events are finally subjected to the same algorithm used to analyze the measured data.

III. RESULTS

A. Dissociation kinematics

For DR channels leading to three fragments, the dissociation kinematics can be represented in a concise way by using the two-dimensional representation $(\eta_1, \eta_2)$ introduced by Dalitz [15]. In the case of the three-body DR of CH$_2^+ + e^-$, which results in two identical hydrogen fragments, the two Dalitz coordinates $(\eta_1, \eta_2)$ are conveniently defined by

$$\eta_1 = \frac{M}{3m_C} \frac{E_H - E_H}{\sqrt{3E}}, \quad \eta_2 = \frac{M}{3m_H} \frac{E_C - 1}{3},$$

where $E_H$ and $E_C$ are the c.m. energies of the individual fragments and $E=E_H+E_H+E_C$ denotes the total kinetic energy release. Each point in the Dalitz plane, which is confined by a circle of radius 1/3 imposed by the energy and momentum conservation, uniquely defines the energy sharing and hence the momenta of the fragments. An alternative representation of the dissociation kinematics is given by the two c.m. angles $\chi_D$ and $\xi_D$, with $\chi_D = \angle (\hat{p}_H, \hat{p}_{H^+})$ denoting the c.m. angle between the final momenta of two H atoms and $\xi_D = \angle (\hat{p}_{H^+}, \hat{p}_{C})$ describing the c.m. angle between the hydrogen with the larger momentum and the final momentum of the carbon fragment. The correspondence between
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FIG. 4. Dalitz plot for three-body final channel following the DR of CH$_2^+$, depicting the correspondence between the Dalitz coordinates ($\eta_1$, $\eta_2$) and the c.m. angles $\xi_D = \angle (\hat{p}_{H}, \hat{p}_{C})$ (solid lines in the left half circle) and $\xi_D = \angle (\hat{p}_{H}, \hat{p}_{C})$ (dashed lines in the right half circle), with H$_+$ denoting the hydrogen with the larger momentum. Note that the Dalitz plot is symmetric around $\eta = 0$.

$(\xi_D, \xi_D)$ and the $(\eta_1, \eta_2)$ coordinates is shown in Fig. 4, taking advantage of the symmetry of the Dalitz plot around $\eta = 0$: The solid lines drawn in the left semicircle represent fixed c.m. angles $\xi_D$, while the dashed lines in the right semicircle reflect discrete c.m. angles $\xi_D$. These two angles also uniquely define the dissociation kinematics; however, the advantage of the Dalitz coordinates is that the Dalitz circle is uniform, i.e., isotropically, filled in case the kinematical phase space is exhausted randomly under no other constraints than energy and momentum conservation.

By selecting DR events with dissociation planes perpendicular to the beam direction, i.e., $|\cos(\theta)| \rightarrow 1$, the kinetic fragment energies $E_i$ and the total kinetic energy release $E$ reduce to the corresponding transversal energies, and $(\eta_1, \eta_2)$ can be approximated by the corresponding transversal Dalitz coordinates $(Q_1, Q_2)$, i.e.,

$$\eta_1 \sim Q_1 = \sqrt{\frac{M}{3m_c}} \frac{d_H^2 - d_{H_1}^2}{\sqrt{3}D^2}$$

and

$$\eta_2 \sim Q_2 = \frac{Mmc}{3m_{H_1}^2} \frac{1}{D^2}. \quad (7)$$

Strictly speaking, we measure in this way the dissociation kinematics in a plane perpendicular to the electron (molecular) beam direction. While no orientation effects are observable at $E_{c.m.} = 0$ for symmetry reasons, the flattened velocity distribution of the electron beam is in principle breaking this symmetry. Such effects, however, are expected to be small and could only recently be observed in a precision measurement of the DR of HD$^+$ [5].

FIG. 5. (Color online) Measured projected distances $D$ for three-fragment events observed in the DR of CH$_2^+$ for orientation angles $|\cos(\theta)| > 0.8$ (solid points). The solid (red) line represents the best fit of the two MC simulated distributions for the C$(^3P)$ [dotted (black) line] and the C$(^1D)$ channel [dashed (blue) line] to the measured spectrum. The dashed-dotted (green) curve shows a simulation of the projected distance distribution expected for the C$(^3P)$ channel when assuming a time resolution of $\sigma_t = 0.0$ ns.

For the finite $|\cos(\theta)|$ interval of $|\cos(\theta)| = 0.8$ employed in the present analysis, a given point $(\eta_1, \eta_2)$ is expected to be smeared out in the $(Q_1, Q_2)$ plane. However, the loss in resolution is found to be small $(\sigma_t \sim 0.01)$. The reason for the limited degradation of the $\eta$ resolution is related to the fact that only relative energies enter into the definition of the Dalitz-coordinates; thus effects caused by the finite length of the electron target, limiting the energy resolution to about 20%, cancel out, and the broadening due to the projection of the fragment energies on the transversal plane is partly suppressed [see also Fig. 6(a)]. Under the present condition of near-zero electron collision energy, we can therefore interpret the measured $(Q_1, Q_2)$ map as an $(\eta_1, \eta_2)$ map of the reaction.

In order to derive the dissociation kinematics for the two three-fragment channels separately we use the proportionality of the total projected distance $D$ to the kinetic energy release. The projected distance distribution $P(D)$ obtained under the restriction $|\cos(\theta)| > 0.8$ is shown in Fig. 5. The C$(^3P)$ and the C$(^1D)$ channel are clearly distinguishable and, even though the two $P(D)$ distributions have some overlap, the separation is good enough to tag the events. The distribution simulated for the C$(^3P)$ channel assuming an infinitely good time resolution (dashed-dotted curve in Fig. 5) shows that the partial overlap of the two channels is caused by the present time resolution of the 3D imaging system, while the width of the $P(D)$ distribution caused by the length of the electron target and the finite $\cos(\theta)$ interval alone would still allow for a complete channel separation. The MC calculations assuming a time resolution of $\sigma_t = 0.9$ ns, a kinetic energy release of $E_{k}(^3P) = 2.62$ eV, and a [C$(^3P)$]:[C$(^1D)$] branching ratio of 70:30 do account very well for the observed spectrum.

The transversal Dalitz plot for the C$(^3P)$ channel was derived by considering only events with $22.5 \text{ mm} \leq D$. 022713-5
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The kinetic energy release was determined to be

\[ E_k(3P) = (2.62 \pm 0.05) \text{ eV} \]

The error given includes the statistical uncertainty as well as systematic contributions, the largest systematic errors being caused by our limited knowledge of the effective length of the interaction region and of the residual energy stored in the

\[ \text{spot separation}. \]

\[ \text{values limited only by the minimum distinguishable light spot separation.} \]

\[ \text{also shown are the c.m. angles } \chi_0 = \angle (\vec{p}_{H}, \vec{p}_{H'}) \text{ (solid lines in the left half-circle)} \text{ and } \xi_0 = \angle (\vec{p}_{H}, \vec{p}_{C}) \text{ (dashed lines in the right half-circle) for some values of } \chi_0 \text{ and } \xi_0. \]

\[ \text{For comparison, a MC simulated distribution for some } (\eta_1, \eta_2) \text{ pairs, smoothed in the same way as the experimental distributions, is shown in Fig. 6(a).} \]

The Dalitz distributions observed for the C(3P) and the C(1D) channel clearly show that the dissociation kinematics of both channels are markedly different from being isotropic and distinctly different from each other, even though the statistics of the C(1D) plot is somewhat limited. Comparison with Fig. 6(a) moreover reveals that the smoothing procedure is only slightly decreasing the resolution and is not influencing the widths of the structures observed in the experimental Dalitz plots (see Sec. IV for further discussions).

**B. Energy releases**

As shown by the simulated \( P(D) \) distributions plotted in Fig. 5, the position of the high energy shoulder of the measured projected distance distribution for the C(3P) channel is independent of the time resolution and is well described by assuming the kinetic energy release to be \( E_k(3P) = 2.62 \text{ eV} \). (Note that the \( E_k \) values given are defined as the kinetic energy releases with respect to the rovibrational ground state of CH3+.)

For a more concise determination of \( E_k(3P) \) we used a projected distance distribution, which was measured employing only the 2D feature of the new imaging setup, i.e., all molecular plane orientations are contributing. From the distribution displayed in Fig. 7, a background spectrum was subtracted, which was derived by selecting events with a c.m. distance \( R_{\text{c.m.}} \) of \( 2\sigma_R \leq R_{\text{c.m.}} \leq 4\sigma_R \) from the beam center, and which was normalized to the measured \( P(D) \) distribution at \( D \geq 31 \text{ mm} \); the intensity of the normalized background distribution amounted to less than a few percent at \( D < 31 \text{ mm} \). Both three-fragment channels are clearly visible in Fig. 7, but as all orientation angles \( \theta \) are contributing, the projected distance distributions of the two-fragment channels are very broad, reaching from the maximum \( D \) value, determined by the total kinetic energy release and the maximum possible event distance \( s \), down to the smallest values limited only by the minimum distinguishable light spot separation.

Fitting the upper end of the \( P(D) \) distribution by MC simulated distributions for the C(3P) channel varying \( E_k(3P) \),
from Fig.7 we therefore used MC simulated 
7, on the other hand, can in principle depend on the details of 
dissociation kinematics, and a fit using the measured instead 
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the two MC simulated distributions for the C 
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rotational motion of the CH2 ions. No dependence of the 
extracted E_k value on the dissociation geometry was ob-
served. As the excitation energy of the C(1D) state relative to 
the C(3P) ground state of C is well known from optical in-
vestigations to be 1.264 eV [13], the E_k(1D) value is thus 
found to be 
\[ E_k(1D) = (1.36 \pm 0.05) \text{ eV}. \]

C. Branching ratio

The branching ratio between the two three-fragment chan-
nels was extracted from the measured projected distance dis-
tributions with and without the orientational cut.

Adjusting the MC simulated P(D) histograms for the two 
channels to the projected distance spectrum for |cos(\theta)|
\( \approx 0.8 \) shown in Fig. 5, a \([C(3P)]:[C(1D)]\) branching ratio of 
70(3):30(3) is obtained, where the error given is dominated 
by the systematic error due to the tail of the C(3P) peak, 
which depends on the time resolution. Because of the cos(\theta) 
cut the line shapes are not expected to be sensitive to the 
dissociation kinematics, and a fit using the measured instead 
of isotropic Dalitz distributions in the MC simulations does 
indeed result in the same branching ratio.

The ungated projected distance distribution shown in Fig. 
7, on the other hand, can in principle depend on the details of 
the dissociation kinematics. To deduce the branching ratios 
from Fig. 7 we therefore used MC simulated P(D) distribu-
tions for the two channels based on the measured Dalitz 
plots. The best fit to the measured distribution results in a 
\([C(3P)]:[C(1D)]\) branching ratio of 65(1):35(1), the error 
being the statistical error only. When using simulated distribu-
tions based on isotropic Dalitz plots, however, the quality of 
the fit decreased only slightly and the resulting branching 

ratio changed only marginally to 66(1):34(1). The branching 
ratio derived from the ungated projected distance distribution 
was found to be sensitive to the minimum distance between 
light spots, causing a systematic error of about \( \pm 3 \). 

Averaging the results obtained from the analysis of the 
gated and ungated projected distance distribution the branch-
ing ratio is found to be 
\[ [C(3P)]:[C(1D)] = 68(4):32(4). \]

IV. DISCUSSION

Some of the results obtained in the present experiment for 
the three-fragment channels of the DR of CH2+e− at E_cm. 
\( \sim 0 \) are at variance with the findings of Thomas et al. [10]: 
For the \([C(3P)]:[C(1D)]\) branching they determined a ratio 
of 51(4):49(5) as compared to 68(4):32(4) deduced in the 

present work. Moreover, for the kinetic energy release in the 
C(3P) channel, a value of \( E_k(3P) = 2.45 \) eV was adopted by 
the authors, which is not only 0.17 eV smaller than the 

present value of \( E_k(3P) = (2.62 \pm 0.05) \) eV, but judged from 

Fig. 10 of Ref. [10] their assumed \( E_k(3P) \) value still seems to 
be too large to describe the high distance edge of their ex-
perimental projected distance distribution. In fact, the \( E_k(1P) \) 
value needed to reproduce the high energy edge of their 
transverse distance data seems to be \( \sim 0.24 \) eV lower than 
ours, while the corresponding edge of the distribution con-
ected with the C(1D) branch would be well accounted for 
using the present value of \( E_k(1D) = 1.36 \) eV. The reason why 
the C(1P) branch in the measurement reported in Ref. [10] is 
found to be a factor of \( \sim 2 \) less intense when compared to the 
C(1D) branch and displays a kinetic energy release which is 
smaller by \( \sim 10\% \) as compared to the results of the present 
experiment is not obvious to us.

On the other hand, the kinetic energy release \( E_k(3P) \) de-
duced in the present measurement is in excellent agreement 
with a value that can be derived from previous photodisso-
ociation and photoionization experiments. Namely, using the 
ionization and dissociation energies measured in the three 

reactions

\[ \text{CH}_2(\tilde{x}IB_1) \rightarrow \text{CH}_2(\tilde{x}IA_1) + e^−, \quad E_i, \]

\[ \text{CH}_2(\tilde{x}IB_1) \rightarrow \text{CH}(3\pi\text{II}) + \text{H}(3S), \quad D_1, \]

\[ \text{CH}(3\pi\text{II}) \rightarrow C(3P) + \text{H}(3S), \quad D_2, \]

with \( E_i = 10.396(11) \) eV [16–18], \( D_1 = 4.33(3) \) eV 
[16, 17, 19], and \( D_2 = 3.465(15) \) eV [20–23], one finds 
\( E_k(3P) = E_i - D_1 - D_2 = 2.60(4) \) eV as compared to \( E_k(1P) 
= 2.62(5) \) eV derived in the present experiment. We would 
like to point out that also the kinetic energy release value for 
the C(1D) channel, which was linked to that of the C(1P) 
channel by the well known \( ^3\text{P} \rightarrow 1\text{D} \) transition energy [13], 
results in a very good description of the high distance edge 
of the projected distance distributions for this channel as 
shown in Figs. 5 and 7.

Based on the weighted average between this and the 

present value, which results in \( E_k(3P) = 2.61(3) \) eV, and the
well known dissociation energies for the hydrogen molecule of 4.478(1) eV [17] and for the CH(X^2Π) molecule as given above, the kinetic energy releases of the two-fragment channels of the DR of CH\textsubscript{2}\textsuperscript{+} are found to be 7.09(3) eV for the C\textsuperscript{(3)P}+H\textsubscript{2}(X^3Σ\textsubscript{g}) and 6.08(3) eV for the CH(X^2Π)+H\textsuperscript{(5)} branch.

In view of a still missing, quantitative model to predict branching ratios for the DR process, statistical model estimates of various sophistication have been used with differing [24], but sometimes also with quite remarkable success [25]. A simple statistical approach, which has been applied with some success to the DR of diatomic molecules [26] and also, e.g., to H\textsubscript{2}O\textsuperscript{+} [9], is to just consider the electronic degeneracies of the final products. This estimate, which neglects any dynamical effects, results in [C\textsuperscript{(3)P}]/[C\textsuperscript{(1)D}]=64:36, in excellent—although maybe fortuitous—agreement with our result, fortuitous because it is obvious from Fig. 6 that the dissociation process does depend also on the symmetry of the final states as reflected by the different dissociation kinematics observed for the two final three-fragment channels.

The Dalitz representation is especially well suited to investigating the kinematical correlation between the three final products. For a purely statistical, phase space dominated DR reaction the Dalitz plot would be evenly populated, which is noticeably not the case for the C\textsuperscript{(3)P} nor for the C\textsuperscript{(1)D} channel; population differences of up to a factor of 3 are observed. Two other reaction extremes are easily recognizable: First, for a true sequential decay via long-lived intermediate complexes the events would be located on well defined kinematical lines. In the DR of CH\textsubscript{2}\textsuperscript{+} a sequential decay of the excited recombinant product CH\textsubscript{2}\textsuperscript{+} can proceed via two paths involving excited H\textsubscript{2} and CH\textsuperscript{+} intermediates, respectively, which should live long enough to decay outside the influence of the third particle and to be able to establish an identity, the latter time scale being governed by the rotational period of the intermediate complex, i.e., \( t_{\text{rot}} \sim 10^{-11} \text{ s} \). Such true sequential decays of CH\textsubscript{2}\textsuperscript{+} via a well defined excited state of the intermediate system will be located in the Dalitz plot on a horizontal straight line with \( \eta_1 = \text{const} \) for the first and on two close to vertical straight lines with \( |\eta_1| \sim \text{const} \) for the second path, where the respective constant is determined by the excitation energy of the intermediate complex. Second, in a truly prompt three-body decay, no time would be available for any rearrangements to occur, and the final state kinematics will reflect the geometrical conformation of the initial molecular ion. As the ground state of CH\textsubscript{2}\textsuperscript{+} is known to be bent by \( \angle (\text{H-cm-H}) \sim 140^\circ \) with only a small barrier to linearity [27], we would expect the events of a prompt three-body decay of CH\textsubscript{2}\textsuperscript{+} to occur around \( \chi_D \sim 140^\circ \) in the Dalitz plot.

A closer inspection of Fig. 6 shows that the actual decay takes place between these two extremes, although likely closer to the latter. Discussing first the C\textsuperscript{(3)P} channel one notices that the main intensity, in qualitative agreement with Ref. [10], is indeed found at \( \chi_D \sim 140^\circ \), but with an energy sharing between the two hydrogen atoms expected in case the dissociation would start with a symmetric, leading to \( \eta_1 \sim 0 \), and an antisymmetric stretching vibration, resulting in \( \eta_1 \sim \pm 0.2 \). A less pronounced maximum in the Dalitz plot of C\textsuperscript{(1)D} is observed at \( (\eta_1, \eta_2) = (\pm 0.20, \pm 0.20) \), which corresponds to \( \chi_D \sim 45^\circ \) and an asymmetric energy sharing between the two H atoms, a decay geometry which does require a considerable angular rearrangement of the hydrogen atoms during dissociation. Unlike the C\textsuperscript{(3)P} branch, the C\textsuperscript{(1)D} channel seems to prefer equal energy sharing between the two hydrogen atoms. Moreover, for the main intensity group the angle between the two hydrogen momenta is smaller, i.e., \( \chi_D \sim 110^\circ – 135^\circ \), and decays with \( \chi_D \leq 90^\circ \) seem to be more likely than for the C\textsuperscript{(3)P} channel.

Minaev and Larsson [28] calculated in a one-dimensional approach potential energy curves for the excited methylene molecule CH\textsubscript{2}\textsuperscript{+} along the linear and the bent reaction coordinates in an attempt to identify the dissociative potential energy curves leading to the three-body dissociation channel. Their main conclusion is that only the 3\( ^3 \)A\textsubscript{2} state, which correlates with the 1\( ^3 \Sigma\textsubscript{g}^- \) state in the linear conformation and which is energetically very close to the dissociation energy, can be responsible for the three-fragment channels in the DR of CH\textsubscript{2}\textsuperscript{+}. Moreover, they argue that the 3\( ^3 \)A\textsubscript{2} state will dissociate to the C\textsuperscript{(3)P} channel at linear structure and to the C\textsuperscript{(1)D} channel for bond angles around \( \angle (\text{H-cm-H}) = 132^\circ \). These conjectures are in qualitative agreement with our findings for the most likely decay pattern. For a more detailed analysis, however, the two-dimensionality of the molecule has to be taken into account for a proper description of the interactions between the various potential energy surfaces and of the dynamics of the process.

V. CONCLUSIONS

Using a 3D-imaging technique, we provide unique kinematic information for the three-body breakup of the methylene ion after dissociative recombination. Selecting events with dissociation planes perpendicular to the beam direction we were able to construct the individual Dalitz plots for the two three-fragment channels and thereby to investigate and to highlight the different dissociation geometries. Furthermore, the branching ratio between the two channels and the kinetic energy release could be determined. The new 3D-imaging technique is found to be well suited to studying the dissociation dynamic of the complete breakup channels in the DR of polyatomic molecular ions.

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