

State selectivity in core ionization of methane

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A clear experimental signature of the population of the lowest triplet state $^3T_1$ of the methane dication is identified in a photoionization experiment. This state is populated only in valence ionization and is absent when the dication is formed by core ionization followed by Auger-Meitner decay. For valence ionization, the total internal energy of the CH_3^+ fragment, formed during the deprotonation of CH_4^{2+} , is evaluated. Notably, the distribution of this internal energy peaks at the same value regardless of the initially populated electronic state of CH_4^{2+} . We find that excited electronic states of CH_3^+ are predominantly populated with significant rovibrational excitation.

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Symmetries and selection rules are the foundation of our current understanding of fundamental physical processes. Studying the dicationic states of atomic and molecular systems populated via valence double ionization and an Auger-Meitner [1] process allows us to gain insight into the relevant selection rules and symmetries for these electron-correlation-driven processes. For example, in case of the Neon atom it can be shown by symmetry arguments that the ^2S term associated to the K -shell hole of Ne^+ , having an electronic configuration of $1s^1 2s^2 2p^6$, cannot relax to the ^3P term of Ne^{2+} , having an electronic configuration of $1s^2 2s^2 2p^4$, by an Auger-Meitner process [2,3]. For molecular systems, it is not clear *a priori* that the rules applicable to atomic systems will be valid directly due to the existence of additional degrees of freedom (vibration and rotation), which would couple to the electronic states, resulting in the breakdown of the Born-Oppenheimer (BO) approximation. Spin symmetry dependence of the Auger-Meitner process was reported earlier for Oxygen, a simple diatomic molecule [4].

Methane, which is one of the smallest molecules having a three-dimensional structure of very high symmetry, can be used as an ideal test bench to advance our understanding of

these processes. However, for CH_4 , a light hydride molecule, the characteristic lifetime of the $1s$ core-hole state [5] is of the order of a few fs, comparable to the characteristic C-H vibration period. Thus, the possibility of coupling between electronic and nuclear degrees of freedom cannot be ruled out. In this sense the Auger-Meitner effect is potentially more complex in a polyatomic molecule than in an atom, not only because the symmetry is different but also because the dynamics due to nuclear motion are more complex.

The methane molecule is isoelectronic to the neon atom, with a deep K shell, an inner valence orbital and three degenerate outer valence orbitals [2], and its ground state configuration is $(1a_1)^2 (2a_1)^2 (1t_2)^6$. The $(1t_2)^{-2}$ configuration of the methane dication, CH_4^{2+} , is associated with four terms, viz., $^3T_1$, ^1E , $^1T_2$, and $^1A_1$, in order of increasing energy.

Several experiments on valence double photoionization of methane are available in the literature [6–8], two of which report the energy of the fragments H^+ and CH_3^+ in coincidence [6,7], as a function of the photon energy over the 35–82 eV range. Among these, the study by Dujardin *et al.* [6] claims that the $^3T_1$ state is populated while the study by Hatherly *et al.* [7] concludes that the $^3T_1$ state is not populated in their experiment. Thus the conclusions drawn from these measurements are not consistent. For the experiment reported by Eland *et al.* [8] where 40.81 eV photons were used and the energy of the two emitted photoelectrons was measured in coincidence, the population of the $^3T_1$ state is identified using the energy of the triplet state obtained from existing literature. Few experimental investigations have used core ionization followed by Auger-Meitner decay to populate and identify the electronic states of methane dication [9–11]. Discussions

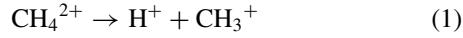
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on the state-selective population of electronic states via an Auger-Meitner process are missing.

Only recently, advanced theoretical methods, working under the BO approximation, have been developed to predict the probability of decay of an initial core-hole state to different possible dicationic states following an Auger-Meitner process [12]. For methane, it was indicated that the triplet ground state ($^3T_1$) of the dication was not produced at all [13,14].

One way to probe the population of dicationic states of methane is to measure the kinetic energy release (KER) spectrum associated with its deprotonation which can be expressed as



The deprotonation of methane dication has posed a question about the role of the initial excitation process in populating the different electronic states available for the dication. When CH_4^{2+} is formed by the impact of a highly charged ion, Ar^{9+} , at low collision velocity, the deprotonation channel shows three distinct contributions in the kinetic energy release distribution (KERD) [15]. This excitation process is primarily associated with the removal of valence electrons from neutral methane. In contrast, when the dication is formed via photon-induced core ionization followed by Auger-Meitner decay, only two contributions are observed in the KERD of the deprotonation channel [11] with the lowest KER contribution being absent. The core-ionization experiment employing fast electrons is less conclusive [10]. The complete KER spectrum is not reported in Ref. [10], where only the average values of fragment kinetic energies are reported for the $(1t_2)^{-2}$ configuration and with a large uncertainty. It is unclear whether the common contributions observed in the KERD for core ionization and valence ionization originate from the same electronic states of the CH_4^{2+} . The lowest-energy contribution which is observed only in the ion-impact experiment [15] is unexplained.

In this Letter we resolve this puzzle and clarify the role of the initial excitation process in the populations of energetically accessible electronic states of the CH_4^{2+} that dissociate via deprotonation. Using photons of two different energies we have measured the KERD of this channel for “valence-ionization” and “core-ionization” processes. Furthermore, we have correlated the results of the experiments with existing *ab initio* calculations [10,11,16] to identify the electronic states populated in both cases. This identification provides (a) a direct correlation between population of the lowest triplet state ($^3T_1$) of methane dication and valence ionization, (b) experimental evidence for state-selective population in the Auger-Meitner decay of the methane cation, and (c) a means to estimate the internal energy of the CH_3^+ molecular fragment generated in the deprotonation process.

The experiment was carried out at the Advanced Light Source (ALS) synchrotron facility at Lawrence Berkeley National Laboratory (LBNL), USA, using the cold-target recoil-ion-momentum spectroscopy (COLTRIMS) technique [17,18]. For the experiment, the COLTRIMS apparatus from the University of Nevada, Reno was attached to ALS beamline 9.0.1, a beamline which provides linearly polarized photons. Two different datasets were collected: 45 eV photons were used for double ionization of valence electrons, and 295 eV

photons were used for Carbon *K*-shell ionization, which is subsequently followed by an Auger-Meitner decay. The COLTRIMS spectrometer uses electric and magnetic fields to guide the cationic fragments and electrons to a pair of position- and time-sensitive delay-line detectors. Once the time-of-flight and position data have been recorded, the three-dimensional momentum and the corresponding energy were calculated for H^+ and CH_3^+ fragments measured in coincidence. These calculations are done using the known values of the electric and magnetic fields, as well as the spectrometer dimensions. The experimental setup has a 4π collection solid angle for electrons up to about 10 eV. In the valence-ionization regime the energies of both emitted electrons were measured while in the core-ionization regime only the energy of the photoelectron (core ionized electron) was measured. The energy of the Auger-Meitner electron is expected to be of the order of hundreds of eV, which is too high to be measured with sufficient resolution and collection efficiency with our experimental setup. The electron energy measurement provides direct information on the populated dication electronic states in the Franck-Condon region if all emitted electrons are detected.

In the data collected with 45 eV photons, the available energy allows the dication to be formed primarily in the $(1t_2)^{-2}$ configuration by valence double ionization [6,14]. The $2a_1^{-1}1t_2^{-1}$ configuration is too high in energy [14] to be populated by 45 eV photons in the Franck-Condon region. Kukk *et al.* [9] reported that the core ionization of methane by synchrotron radiation yields a CH_3^+ fragment originating only from the $(1t_2)^{-2}$ configuration of CH_4^{2+} [9]. Hence in our core-ionization experiment with 295 eV photons, only the $(1t_2)^{-2}$ electronic configuration of the CH_4^{2+} feeds the deprotonation channel.

The energy correlation map obtained for valence ionization is shown in Fig. 1. Three distinct regions are clearly visible in the energy correlation map of KER with the electron energy sum ($E_{e1} + E_{e2}$) and these appear to be anticorrelated, i.e., the lowest KER has the highest value of the ($E_{e1} + E_{e2}$) and vice versa. The expected ($E_{e1} + E_{e2}$) values for the four relevant electronic states belonging to the $(1t_2)^{-2}$ configuration of CH_4^{2+} are also marked on this figure, indicating that primarily the states $^3T_1$, ^1E , and $^1T_2$ are populated in our experiment on valence double ionization.

Figure 2 shows a comparison of the KERD obtained using 45 and 295 eV photons. It clearly demonstrates that the core-ionization process does not yield the low KER peak but only the higher two, in contrast to valence ionization. Thus, there is a certain selectivity observed in the case of core ionization. For reference, data from an earlier ion-impact ionization study [15] are also shown on the same graph. In this earlier report [15], it was proposed that the highest-energy contribution to the KERD results from the population of the $^1T_2$ state of the CH_4^{2+} .

In order to identify the electronic states of the CH_4^{2+} that were populated in our valence-ionization experiment, we considered the spectrum of the total energy carried by the two photoelectrons ($E_{e1} + E_{e2}$) subtracted from the energy of the ionizing photon (45 eV). Such a spectrum is shown in Fig. 3 for the total KERD and, also, for three different regions of the KERD, viz., (i) $\text{KER} < 5.14$ eV, (ii) 5.14 eV $< \text{KER} <$

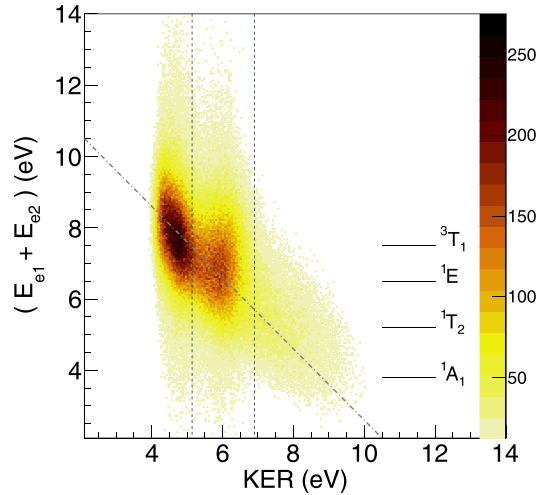


FIG. 1. Energy correlation map for deprotonation of CH_4^{2+} : Yield as a function of KER and $(E_{e1} + E_{e2})$ for valence double ionization using 45 eV photons. The vertical dashed lines indicate selected regions of KER and the dashed-dotted line indicates a constant value for $[\text{KER} + (E_{e1} + E_{e2})]$. The horizontal lines mark the expected $(E_{e1} + E_{e2})$ for the four lowest states of CH_4^{2+} corresponding to the $(1t_2)^{-2}$ configuration (see text).

6.9 eV, and (iii) $\text{KER} > 6.9$ eV, marked on Fig. 1 for clarity. These regions are chosen to minimize the overlap between different KER contributions.

Taking the zero-point energy of neutral methane (≈ 1.19 eV) [19] into account, we used the vertical excitation energies reported in Ref. [10] to locate the positions for the electronic states of the CH_4^{2+} populated by vertical Franck-Condon transitions from the ground state of neutral methane in its tetrahedral T_d geometry. A comparison of the spectrum shown in Fig. 3 with these *ab initio* calculations indicate that the three lowest electronic states, $^3T_1$, ^1E , $^1T_2$ of CH_4^{2+} , are predominantly populated in our experiment under the valence-ionization regime. Moreover, the three contributions observed in the KERD can be correlated to

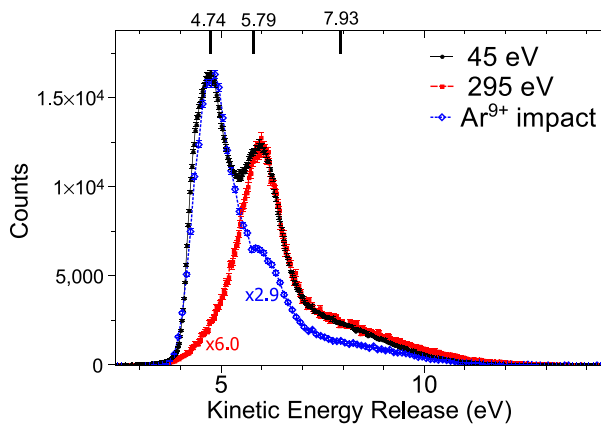


FIG. 2. KER spectra for deprotonation of CH_4^{2+} at two different photon energies. Data from an earlier ion-impact ionization study [15] is also shown for reference. The ticks at the top locate the peak positions from the three-Gaussian fit in Ref. [15].

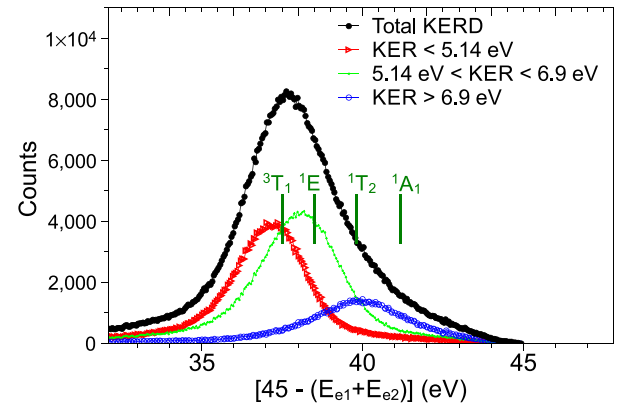


FIG. 3. Spectrum of the total energy carried by the photoelectrons $(E_{e1} + E_{e2})$ subtracted from the energy of the excitation photon (45 eV) for the valence-ionization regime, for total KERD, and selected regions of the KERD. The ticks indicate the location of the four lowest electronic states of the CH_4^{2+} in the $(1t_2)^{-2}$ configuration taken from Ref. [10].

the dicationic states $^3T_1$, ^1E , $^1T_2$, respectively, in order of increasing energy. A small mismatch is observed between the centroid of the electron sum energy distributions and the values expected from these *ab initio* calculations. This could be due to uncertainty in the theoretical calculation and/or from the overlap of the different peaks of the KERD which hinders a clean separation. Nevertheless, the lowest-energy contribution to the KERD of the deprotonation channel can be attributed, with confidence, to the population of the lowest triplet state, $^3T_1$, of the CH_4^{2+} formed by valence ionization.

To address the populated electronic states in the “core-ionization regime,” we determined the mean values of the different contributions to KERD by fitting a sum of three and two Gaussian distributions to the KERD obtained for the 45 and 295 eV excitations, respectively. The results of these fits are summarized in Table I. It is noted that the mean values are in very good agreement for the two data sets, indicating that the same electronic states are likely to be populated. Williams *et al.* [11] have reported that for core ionization of methane resulting in the population of the deprotonation channel, the dominant peak of the KERD, located at ≈ 5.8 eV, is correlated with the lowest excited singlet state (^1E) of the CH_4^{2+} . This is in good agreement with the assignment of the ^1E state to the KERD contribution with a mean value of ≈ 5.8 eV in our experiment for the case of valence ionization. It is also the case for the highest-energy contribution to KERD of the deprotonation channel, which may be assigned to the ($^1T_2$) dicationic electronic state for both core and valence

TABLE I. Values of the mean energies and full widths at half maxima (FWHM) of the Gaussian distributions used to fit the experimental KER spectra. The relative error in the fitted values is $< 5\%$. All values are in eV.

E photon	$\bar{E}_I$ (FWHM)	$\bar{E}_{II}$ (FWHM)	$\bar{E}_{III}$ (FWHM)
45	4.6 (0.8)	5.8 (1.4)	7.6 (3.2)
295		5.9 (1.5)	7.7 (4.1)

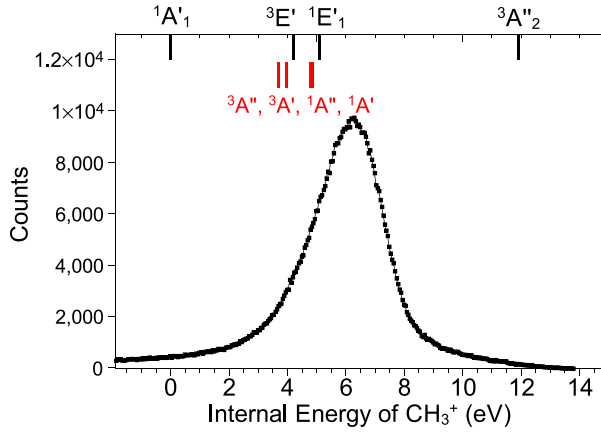


FIG. 4. Internal energy distribution for the CH_3^+ molecular ion formed after valence double ionization of methane. The lowest electronic energy levels of the CH_3^+ ion taken from Ref. [10] (black lines) and Ref. [16] (red lines) are indicated at the top.

ionizations. The absence of any contribution from the lowest electronic state associated with the triplet $^3T_1$ term, indicates spin selectivity in the Auger emission process. In a recent *ab initio* investigation of the Auger-Meitner spectrum of methane [14], Matz *et al.* reported “zero” probability for populating the triplet state $^3T_1$ of the $(1t_2)^{-2}$ configuration. This theoretical prediction is in agreement with our experimental observations.

To gain insight into the possible final states of the CH_3^+ molecular ion, we calculated the energy difference between the photon energy (45 eV) and the total kinetic energy carried by all particles emitted in the valence-ionization process. The energy difference ΔE is given by the equation

$$\Delta E = (h\nu) - (\text{KER} + E_{e1} + E_{e2}) \quad (2)$$

To determine the total internal energy (E_{int}) of the CH_3^+ fragment (which is the sum of its electronic, vibrational, and rotational energy), ΔE has to be shifted by the energy difference, E_{gs} , between the ground electronic state of the CH_3^+ ion and the neutral methane molecule, explicitly expressed as

$$E_{\text{int}} = \Delta E - E_{\text{gs}} \quad (3)$$

The value for $E_{\text{gs}} \approx 26.2$ eV can be obtained by using *ab initio* calculations of the ground electronic states [10] and taking into consideration the zero-point energies of the neutral methane molecule (≈ 1.19 eV) [19] and the methyl cation (≈ 0.86 eV) [16].

The distribution of the internal energy (E_{int}), as calculated from Eqs. (2) and (3), is depicted in Fig. 4 and shows a single broad peak, indicating that the kinetic energy sum ($\text{KER} + E_{e1} + E_{e2}$) is approximately constant. The energy of the ground and the first few excited electronic states of CH_3^+ are also indicated on the top of Fig. 4. The energy values in the planar D_{3h} symmetry are taken from the *ab initio* calculations of Flammini *et al.* [10] and correspond to the electronic states $^1A_1'$, $^3E'$, $^1E_1'$, and $^3A_2'$. Under the fully relaxed C_s symmetry, the lowest triplet and lowest excited singlet degenerate states ($^3E'$ and $^1E_1'$, respectively) are split due to the Jahn-Teller effect and four electronic states are reported, viz., $^3A''$, $^3A'$, $^1A''$, and $^1A'$ [16]. The primary electronic states expected to be

populated at the dissociation limit are the ones having energy less than ≈ 6.3 eV, which correspond to the peak value of the measured distribution shown in Fig. 4. The dissociation energy required for the formation of fragment pairs (CH_2^+ , H) and (CH^+ , H_2) from the CH_3^+ ion is of the order of 5.40 and 5.44 eV, respectively [20], which is about ≈ 0.9 eV less than the peak value of this measured distribution. Thus from Fig. 4 we can conclude that the detection of CH_3^+ in its ground state $^1A_1'$ is much less probable in our experiment as the ions formed in this state will likely dissociate. Among the other possible states, the most probable value of the rovibrational energy for the lowest triplet state ($^3A''$) [16] is ≈ 2.6 eV while this value for the lowest excited singlet state ($^1A''$) [16] is ≈ 1.5 eV, in the valence-ionization regime. These results are likely to be useful for the astrophysical community as the methyl cation is considered a pivotal astrochemical species [21] and has also been recently detected in a protoplanetary disk [22].

Furthermore, to discuss the pathways connecting the initial states of CH_4^{2+} with the final states of CH_3^+ , we take advantage of the potential energy landscape along the C-H stretch coordinate reported in Ref. [11]. As per this calculation, when a single C-H bond is stretched, the $^3T_1$ and ^1E states of CH_4^{2+} populate the fully relaxed (having C_s symmetry) lowest triplet state and the first excited singlet state of the methyl cation, respectively. This calculation also indicates that an initial population of the $^3T_1$ and ^1E states of CH_4^{2+} may populate the ground state $^1A_1'$ of the methyl cation (having D_{3h} symmetry) via an intersystem crossing and a conical intersection, respectively. The calculated KER value reported for the transition from the $^3T_1$ state of CH_4^{2+} to the $^1A_1'$ state of CH_3^+ is 10.45 eV while for the transition from the ^1E state of CH_4^{2+} to the $^1A_1'$ state of CH_3^+ is 11.25 eV. These calculated values are much higher than the corresponding values measured in the experiment for the population of the $^3T_1$ and ^1E states of CH_4^{2+} . The possibility of high internal rovibrational excitation in the $^1A_1'$ state of CH_3^+ may lead to the lowering of these calculated KER values, but such internally hot CH_3^+ ions may dissociate further and not get detected in our experiment as intact CH_3^+ ions. Our experimental results indicating a low probability of detection of CH_3^+ in its ground state $^1A_1'$ is in agreement with this prediction.

Additionally, our results are consistent with the results reported in Ref. [23] where it is shown that the yield of the fragment pair (CH_2^+ , H^+) relative to the yield of the fragment pair (CH_3^+ , H^+) becomes greater than unity for photon energies above 50 eV. It is speculated by the authors that this increase is likely due to either a three-body fragmentation of CH_4^{2+} into (CH_2^+ , H^+ , H) or due to the secondary decay of CH_3^+ into the fragment pair (CH_2^+ , H). In our experiment with 45 eV photons, the ratio of the yield of the fragment pair (CH_2^+ , H^+) relative to the yield of the fragment pair (CH_3^+ , H^+) is ≈ 0.73 .

In conclusion, we have provided direct experimental evidence for the state-selective population of available electronic states in a core-ionization experiment, for the highly symmetric methane molecule. This is in agreement with the theoretical prediction validating the use of BO approximation and indicating that the coupling between the electronic and nuclear degrees of freedom is insignificant in the

Auger-Meitner decay of this molecule. Furthermore, our work on valence ionization has established the correlation between the lowest-energy contribution observed in the KERD of the deprotonation channel of methane dication to the population of its lowest triplet state $^3T_1$. By comparing the electronic states of CH_4^{2+} populated by “valence ionization” with those populated via “core ionization,” it is shown that the lowest triplet state $^3T_1$ of the $1t_2^{-2}$ configuration of the CH_4^{2+} is populated only via valence ionization and not via core ionization.

Moreover, by considering the energy balance of the dissociation process following valence ionization, we determined the distribution of the internal energy carried by the CH_3^+ ion formed during the deprotonation of CH_4^{2+} and found it to be of the order of few eV's ($\approx 3\text{--}9$ eV). The evidence clearly indicates that the CH_3^+ fragments resulting from deprotonation following valence ionization are predominantly populated in their lowest triplet and first excited singlet states (and not in the electronic ground state, $^1A'_1$), with both electronic states being rovibrationally excited. The former mainly originates from populating the $^3T_1$ state of the transient CH_4^{2+} , while the latter arise mostly from populating the ^1E state.

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There are no conflicts of interest to declare.

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