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X-ray photochemistry of carbon hydride molecular ions

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Electronic Supporting Information

The experiment was performed at the PLEIADES beam line of SOLEIL synchrotron radiation facility with the merged beams setup described in[1]. The CH_2^+ ions were produced in an ECR ion source from dissociation of methane. After extraction and selection by a dipole magnet, typical ionic currents of 50 nA were available in the interaction region. A second dipole magnet analyzed the charge and mass of the fragments after interaction. Fig. 1 displays the variation of the C^{2+} fragment counting rate as a function of photon energy in the 280-310 eV photon energy range. The absolute scale was obtained by assuming that the direct photoionization cross section at 310 eV has the same intensity for CH_2^+ and C^+ ions[1].

For the two lowest transitions of CH_2^+ we estimate the decay channel C^{2+}/H/H to be only 3% of the overall products. In order to compare with the experiment we multiplied the computed x-ray absorption cross sections by the branching ratio of this channel. The comparison with the experiment is shown in Fig. 1. Furthermore, since we do not compute the branching ratio for the higher lying core-excited states, we can only compare the computed x-ray absorption cross sections below 290 eV. Given the larger statistical uncertainties of our calculations for weak channels, the agreement between the experimental spectrum and the calculations is satisfactory. The unscaled absorption cross sections for the other transitions are shown in shaded area for comparison. It should be noted that the branching ratio of the C^{2+}/H/H for each band can be estimated from this comparison.

The electronic processes considered in this work are depicted as energy level diagrams in Fig. 2 and 3 for $CH^+{}_2$ and CH_3^+, respectively. In Fig. 4, the energy of the dicationic states at the ground state equilibrium geometry of each system is given with respect to the energy of the corresponding electronic ground state. The latter were obtained from Hartree-Fock calculations. The energies of the dicationic states are taken from the CI calculations for the Auger decay.

References

1 J.-P. Mosnier, E. T. Kennedy, P. van Kampen, D. Cubaynes, S. Guilbaud, N. Sisourat, A. Puglisi, S. Carniato and J.-M. Bizau, *Phys. Rev. A*, 2016, **93**, 061401.

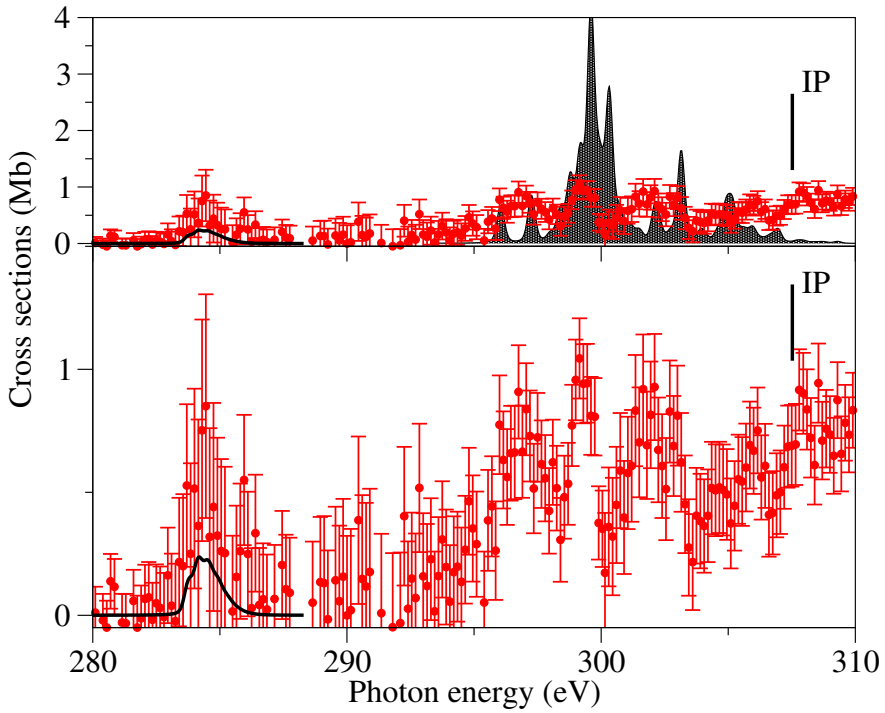

Fig. 1 Absolute partial x-ray absorption cross sections in CH_2^+: only the $C^{2+}/H/H$ fragmentation channel is detected after x-ray absorption (red dots). The computed spectrum (full black line) is thus the total x ray absorption cross sections multiplied by the branching ratio of the $C^{2+}/H/H$ channel. The computed spectrum was globally shifted such that the lowest peak coincides with experiments. Ionization threshold is indicated by the vertical black bar. In the top panel, the shaded area shows the unscaled x ray absorption cross sections above 290 eV for comparison.

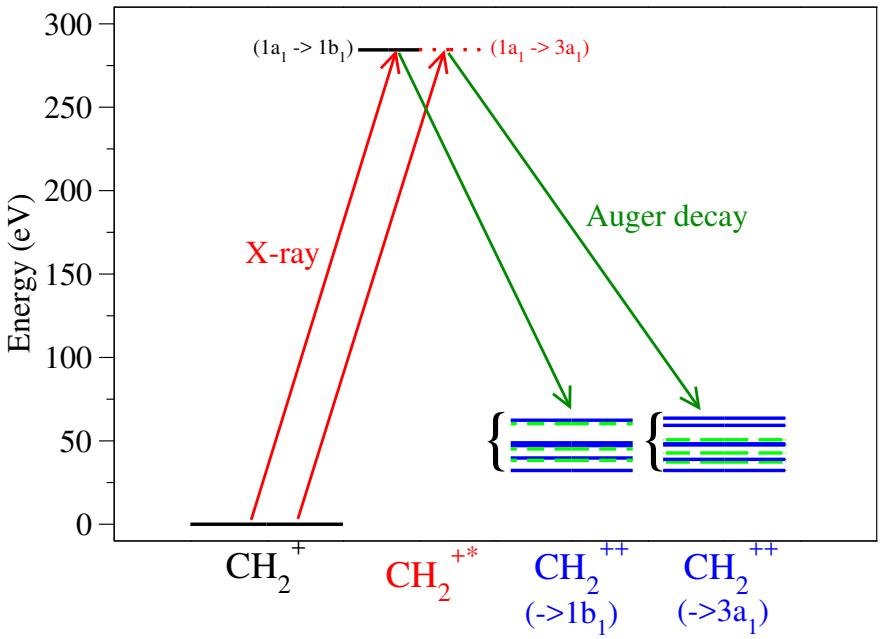

Fig. 2 Energy level diagram of the electronic processes considered in this work,for CH_2^+. The energies are given at the ground state equilibrium geometry.

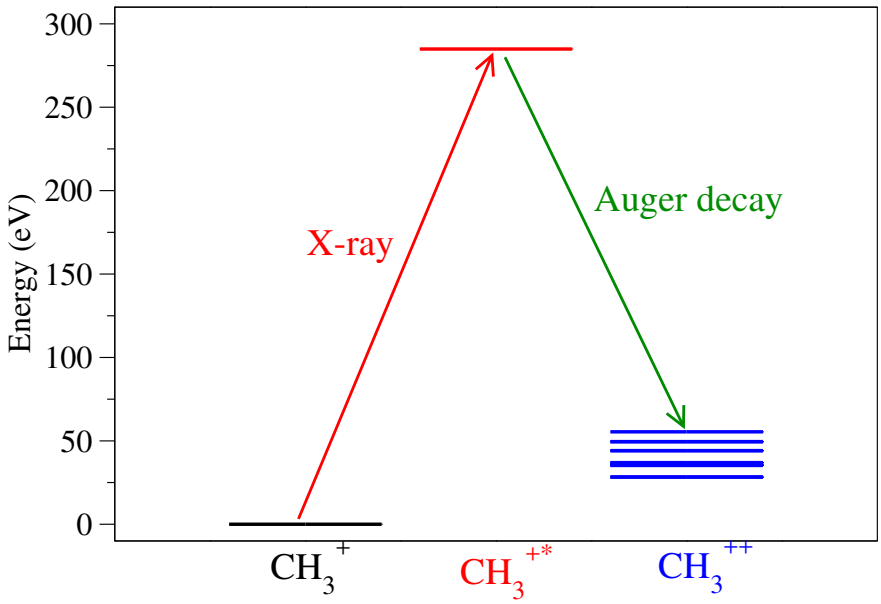

Fig. 3 Energy level diagram of the electronic processes considered in this work, for CH_3^+. The energies are given at the ground state equilibrium geometry.

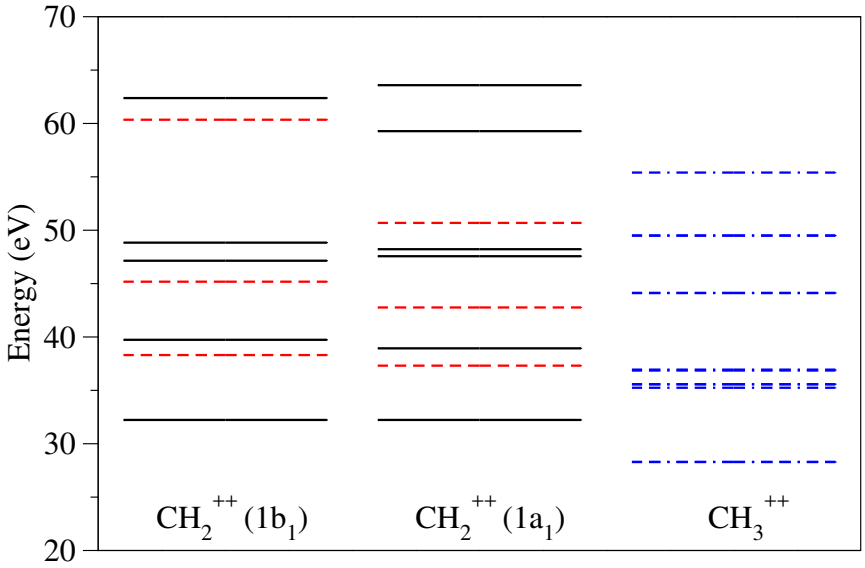

Fig. 4 Energy of the dicationic states, populated in the Auger decay, at the ground state equilibrium geometry for CH_2^+ and CH_3^+. Full black lines correspond to singlet states of CH_2^{++}. Triplet states of CH_2^{++} are shown with red dashed lines. Blue dashed-dotted lines represent doublet states of CH_3^{++}.