Absence of Triplets in Single-Photon Double Ionization of Methanol

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ABSTRACT: Despite the abundance of data concerning single-photon double ionization of methanol, the spin state of the emitted electron pair has never been determined. Here we present the first evidence that identifies the emitted electron pair spin as overwhelmingly singlet when the dication forms in low-energy configurations. The experimental data show that while the yield of the CH$_2$O$^+ + H$_3$ ground state was largely absent. According to high-level ab initio simulations, these facts indicate that photoionization promptly forms singlet dication states, where they quickly decompose through various channels, with significant H$_3$ yields on the low-lying states. In contrast, if we assume that the initial dication is formed in one of the low-lying triplet states, the ab initio simulations exhibit a metastable dication, contradicting the experimental findings. Comparing the average simulated branching ratios with the experimental data suggests a >3 order of magnitude enhancement of the singlet:triplet ratio compared with their respective 1:3 multiplicities.

Photoionization is one of the basic types of light–matter interaction. The most intensely studied and implemented scenario is the single-photon-induced emission of an electron at a rate that is linear with light intensity. In contrast, there are several types of photoemission processes in which one photon induces the emission of two (or more) electrons. These are classified by the excitation mechanism, for example, the Auger decay or the interatomic Coulombic decay following ionization of a core electron. A less well-understood category of single-photon double ionization (SPDI) is the concerted removal of two valence electrons by a single EUV photon that relies on electron correlations. In molecular systems, intramolecular charge migration on the attosecond time scale initiated by SPDI affects the molecular dynamics and Coulomb explosion (CE) that follow on the femtosecond time scale. SPDI is closely related to the single-photon-induced multielectron generation (MEG) phenomenon appearing in solids and quantum-confined nanostructures and affecting the efficiency of solar cell devices.

The determination of the spin state of the ejected electrons in SPDI is central to understanding the process, but its determination is a challenge. Some SPDI studies have exploited symmetry for determining the total spin state of the emitted electrons. For example, in isolated centrosymmetric systems, the ejected electron pairs in triplet-ungerade or singlet-gerade wave functions exhibit a node at the so-called “Wannier point” and are therefore less likely to be produced by SPDI. This propensity rule was supported by observation of the electronic state of the remaining dication. Gaire et al. compared the near-threshold double photoionization of two centrosymmetric systems, acetylene and ethylene, using the measured photoelectron energies and photo-ion masses to determine the final state of the dication. For the acetylene dication, a highly populated metastable $^3\Sigma^+$ ground state was found, while for ethylene, the metastable $^1\text{A}_g$ ground state was barely populated. These results were in accordance with the propensity rule. However, in molecules that are not centrosymmetric, little is known about the total spin state formed in the SPDI processes. For example, SPDI measurements in methanol, among other noncentrosymmetric systems, were assigned to both singlet and triplet states of the emitted electron pair. This approach was adopted also by our previously published calculations of the methanol dication singlet and triplet potentials at fixed geometries as a function of the C–O stretch, which suggested similar CT barriers for both singlet and triplet states.

In the absence of inversion symmetry and very similar energetics in the Franck–Condon (FC) region, a 1:3 singlet:triplet ratio was tentatively suggested according to their respective multiplicities. In this paper, we focus on the spin state of the electron pair emitted in SPDI of methanol and find that previous assumptions about the spin propensities are not valid. In view of the absence of symmetry and the difficulties in direct measurements, we rely on non-adiabatic ab initio molecular dynamics (NA-AIMD) simulations as the primary tool for analyzing the experimental results. We have shown recently...
that NA-AIMD simulations of the methanol singlet dication manifold successfully reproduce the experimental CE branching ratios, kinetic energy release (KER), and three-body momentum correlations, initiated by an ultrafast EUV pulse.25 High-lying excited states of the dication formed in SPDI were found to be responsible for the C–O bond cleavage, either by rapid non-adiabatic electron transfer or by ultrafast proton migration from the doubly ionized methyl part to the OH, while in the low-lying states, the initial charge localization on the methyl part and a charge-transfer (CT) barrier prevent the C–O bond cleavage on the low-lying states, resulting in more complex dynamics, including the formation of H3+ via a roaming H2 mechanism. The movie provided in the Supporting Information compares two typical singlet and triplet ground state trajectories, both initiated with the same phase-space configuration. While the triplet remains stable for >1.5 ps of the NA-AIMD simulation, the longest-lived singlet trajectory dissociates after less than ~400 fs due to the ultrafast roaming H2 dynamics.28 This in agreement with time-resolved experimental studies.25,28 In contrast, all of the 100 NA-AIMD trajectory simulations performed on the triplet ground state were found to resist CE.

In Figure 1, we show the relative energetics of the singlet and triplet ground state potentials at different molecular geometries. At the Franck–Condon (FC) geometry, the triplet manifold’s ground state lies slightly below that of the singlet. Both triplet and singlet states exhibit similar ~3 eV CT barriers, effectively preventing the C–O bond’s cleavage from forming the CH3+ + OH+ products. On the singlet ground state, the formation of H3+ + COH+ is energetically favorable and proceeds efficiently via the roaming H2 mechanism.46–49 Here, a neutral H2 separates from a HCOH2+ dication decays by competing channels of proton capture, forming H3+, and long-range electron transfer (“inverse harpooning”), forming H2. Here.25,27,49 When considering the triplet state energetics along a possible roaming H2 pathway, we need to remember that H2 is stable only in its singlet state, hence requiring a triplet HCOH2+. As shown in Figure 1, the optimized HCOH2+ triplet state lies over ~5.9 eV above that of the singlet, posing an ~3.7 eV barrier that prevents triplet methanol dications formed in the FC geometry from dissociating via the roaming H2 mechanism. In comparison, singlet HCOH2+ + H2 lies ~2.8 eV below the singlet FC geometry, resulting in energetically favorable roaming H2 dynamics.

As predicted by Luzon et al.,45 similarly to the high-lying singlet states, high-lying triplets can fragment via cleavage of the C–O bond, eliminating metastable trajectories. However, although H3+ is observed to form on excited states of the triplet manifold (via nonroaming dynamics), H3+ was not formed in any of the 700 trajectories simulated on the ground state and the first six excited states of the triplet manifold. In Table 1, we summarize the probabilities for formation of H3+ and methanol dication CH3OH2+ in its singlet and triplet states.

### Table 1. Comparison of Experimentally Measured and State-Resolved Theoretically Simulated Branching Ratios for the H3+ + COH+ Coulomb Explosion and the Metastable CH3OH2+ Dication

|                  | H3+ + COH+ (%) | CH3OH2+ (%) |
|------------------|----------------|-------------|
| **Theory**       |                |             |
| singlet (GS, first, second, third, fourth–sixth) | 34, 21, 7, 0, 0 | – |
| triplet (GS, first, second, third, fourth–sixth) | – | 99, 41, 6, 0, 0 |
| **Experiment**   |                |             |
| undeuterated     | 6 ± 0.5        | <1          |
| deuterated6      | 8 ± 0.5        | <0.035      |

*Corresponding deuterated ions.*

The exclusive production of H3+ on singlet states and metastable dications on triplet states opens an opportunity for experimental determination of the singlet-triplet ratio in the SPDI of CH3OH. However, the 32/2 mass over charge ratio of the methanol dication is accidentally equal to that of the O+ ion. Nevertheless, three-dimensional (3D) fragment imaging allows us to detect the momentum of each ion as well as the mass/charge ratio of the photoionization product based on the time-of-flight measurement. Figure 2a shows the momentum distribution of the parent CH3OH+ ion measured in the X–Y plane of the microchannel plate (MCP) detector. The red ellipse indicates ions originating from the molecular beam, which are moving in the Y direction of the lab frame. The dashed magenta circle indicates the momenta of CH3OH+ ions, shown by the isotropically oriented distribution compared to that of the skinned molecular beam. In contrast, Figure 2b shows the momentum distribution measured for a mass/charge ratio of 32/2 corresponding to either metastable CH3OH2+ dications or O+ fragments. Clearly, the signal is dominated by the O+ product of dissociative ionization, whose recoil results in the observed broad momentum distribution.

To disentangle the metastable CH3OH2+ signal, we take advantage of the negligible recoil of the parent ion due to electron ejection. Metastable CH3OH2+ ions originating from the molecular beam are expected to exhibit a momentum distribution similar to that of the CH3OH+ ions, shown by the red ellipse in Figure 2a. Furthermore, we can subtract an average background of low-recoil fragments, estimated from the regions indicated by the dotted black ellipses in panels a and b of Figure 2. The blue line in Figure 2c shows the mass/
charge spectrum of the total ion yield × 1/50, where the red line shows the background-subtracted spectrum of ions formed with no recoil from the molecular beam. Both spectra are normalized to the total yield of CE channels that include CO bond cleavage, H₃⁺ formation, and different three-body CE channels. The background-subtracted mass spectrum exhibits residual contributions from low-KER OH⁺ and O⁺ (or CH₃OH²⁺), allowing determination of an upper limit of <1% probability for the formation of a metastable methanol dication in single-photon double ionization. In comparison, H₃⁺ formation is observed at ∼6% of all CE events, in agreement with the results of Luzon et al. To remove the residual uncertainty due to low KER O⁺ yields, we performed the same study using deuterated CH₃OD methanol. Panels a and b of Figure 3 show the momentum distributions corresponding to mass over charge values of 33 and 33/2, which can be distinguished from singly ionized products. Note the 50-fold lower yield color scale values for a 33/2 mass/charge ratio compared with Figure 2b, both normalized to the respective singly ionized parent cation yields. Due to the improved signal-to-noise ratio and statistics of the CH₃OD measurement, the low KER O⁺ peak is clearly visible in the mass spectrum shown in Figure 3c, showing a distinguishable splitting between O⁺ fragments ejected toward or away from the MCP detector. As the deuterium is on the hydroxyl part, we assume a negligible isotope effect on the singlet:triplet ratio, roaming H₂ or proton capture from the methyl part. Nevertheless, deuteration may affect the probability of the roaming H₂ to capture the H/D of the hydroxyl.

Assuming an equal population of the simulated states listed in Table 1, the average H₃⁺ formation probability is expected to be ∼10% on the singlet states, in rough agreement with the experimental branching ratio. No H₃⁺ formation is expected on the triplet manifold. In contrast, metastable dications are expected to form with an average ∼20% probability on an equally populated triplet manifold. Thus, assuming a single-t:triplet ratio of 1:3 would result in six metastable cations for each H₃⁺ + COH⁺ CE event. In contrast, the experimental data of the deuterated system show fewer than one metastable cation for more than ∼200 triatomic hydrogen ions. This indicates a >3 order of magnitude enhancement relative to the tentatively expected singlet:triplet ratio according to their 1:3 multiplicities. This surprising selectivity for single-photon double ionization of a noncentrosymmetric system suggests the possibility of new selection rules for single-photon double ionization. Nevertheless, it is important to note that while the NAIMD simulations exhibit a stable dication up to 1.5 ps, the experimental setup cannot distinguish between instantaneous dissociation and delayed dissociation on a nanosecond time
scale due to the finite acceleration time. Thus, a particularly efficient intersystem crossing, which is beyond the scope of the theoretical work presented here, could in principle quench the metastable dication. However, in the case of such significant intersystem crossing, the branching ratios, KER, and three-body momentum correlation distributions can be expected to reflect the landscape of the intersystem coupling and be quite different from the simulated singlet manifold dynamics that successfully reproduce the experimental data when initiated from the FC region.

The presented singlet:triplet ratio enhancement in the single-photon double ionization of methanol provides insight into the electron—electron correlations induced in the SPDI process in the absence of inversion symmetry. The EUV photon energies produced by the HHG source lie high above the SPDI threshold, reaching ~100 eV photons. Thus, these findings are not limited to a narrow window of photon energies. Future theoretical work is needed to investigate SPDI electron—electron correlations and describe the relative contribution of different excited states and to perform estimation of the possible intersystem crossing effect on the dication dynamics. The generality of the observed spin state selectivity can be further tested as suppression of roaming H2 dynamics on the triplet dication can be expected to play an important role also for other organic molecules that often exhibit formation of H3+ via roaming H2 dynamics. Furthermore, double ionization by a strong-field laser, as opposed to ionization by a single EUV photon, may exhibit formation of metastable methanol dications and reveal different correlations between the ejected electrons.

### EXPERIMENTAL AND COMPUTATIONAL METHODS

The experimental setup for single-photon Coulomb explosion imaging and theoretical NA-AIMD simulations have been described previously. Briefly, broad bandwidth ultrafast EUV pulses are produced by high-order harmonic generation (HHG) in a semi-infinite neon gas cell. The resulting EUV pulses are spatially filtered from the higher divergence near IR and cross a skinned effusive beam of commercially available CH3OH or CH3OD samples. The cationic products are accelerated, and their coincidence 3D momenta are imaged on a time and position sensitive detector. True CE events are disentangled from an overwhelming dissociative ionization background based on the total momentum conservation of two coincident hits on the detector.

Theoretical NA-AIMD simulations were performed using CASPT2 potentials. Non-adiabatic dynamics were approximated using surface-hopping molecular dynamics trajectories generated at the XMS-CASPT2(8e,8o)/aug-cc-pVDZ level using the BAGEL electronic structure package. A more detailed description of the NA-AIMD is provided in our previous work concerning the CE dynamics on the singlet manifold of methanol dication states. To determine the relative probability of different double-ionization product channels, for each dication state, we initiate 100 trajectories from different initial phase-space configurations. These were sampled from neutral ground state AIMD simulations at 300 K, performed on the CASSCF level using the MOLCAS package.

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