Supporting Information

Summary of Content:

1) Experimental setup

The experimental setup is detailed in Ref. [1] and is schematically shown in Figure S1. The 10-kHz PULSAR laser in the J.R. Macdonald Laboratory at Kansas-State University provided a beam of about 20 fs pulses at a central wavelength of 785 nm. The laser beam, the intensity of which was controlled by a rotatable neutral density filter, was focused into a thick-lens velocity-map imaging (TL-VMI) spectrometer[2] inside the experimental chamber by a 50 cm focusing mirror, where it intersected a beam of C_{60} molecules. The long focal length was chosen to maximize the volume of C_{60} molecules in the laser focus. The C_{60} molecular beam was generated by heating highly purified C_{60} soot (sublimed, 99.9% from Sigma Aldrich) in a home-built oven at a temperature of about 500-600 °C. The resulting photoelectrons after laser-fullerene interaction are projected by the electrostatic lens of the TL-VMI onto a micro-channel plate (MCP) / phosphor screen assembly. The fluorescence on the phosphor screen is recorded by a Peltier-cooled charge-coupled device (CCD) camera (Sensicam QE, PCO). Large focusing volume, high laser repetition rate and long data acquisition time were required to obtain sufficient statistics for the low laser intensities. The residual gas pressure in the experimental vacuum chamber is kept at 10^{-10} Torr to maintain a low background signal level. The detected VMI images are Abel-inverted[3] to extract the 2D-momentum distribution in the $p_z = 0$ plane, where the convention is that the detector lies in the xy-plane with the laser polarization along the y-axis and the laser propagating along the x-axis. The z-axis is perpendicular to the detector plane. The peak intensities in the focal volume are estimated by measuring the above threshold ionization (ATI) electron emission from Xe under identical experimental conditions[4].

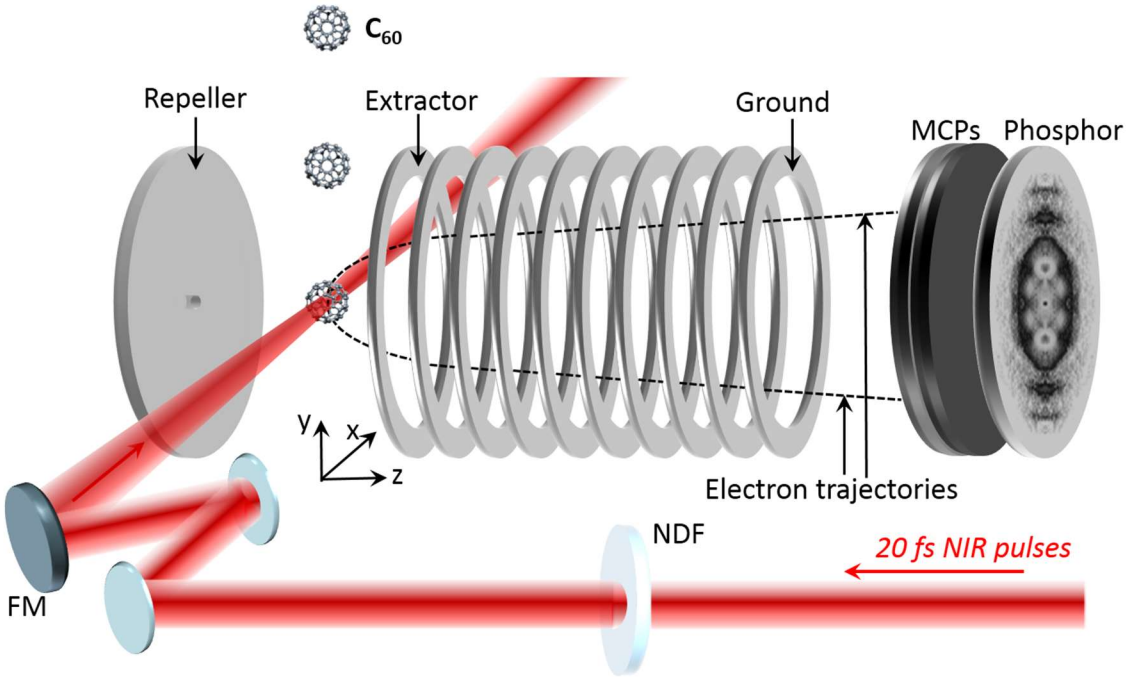

Fig. S1. A schematic drawing of the experimental setup. MCPs: micro-channel plates; FM: focusing mirror; NDF: neutral density filter.

2) Excitation mechanisms of the SAMO and Rydberg states

The SAMO and Rydberg states are not optically active, their transition dipole moments with the ground state is zero (Fig. S2a). Therefore, they cannot be directly accessed from the ground state during the pulse. However, these states can be populated by vibronic coupling or dipole coupling to optically active excited states. As can be seen on Fig. S2a, there are only two bands of valence state below the band of *p*-SAMO that can be accessed directly from the ground state during the pulse. The second band of optically active states is within 0.1 eV of the *p*-SAMO band, so vibronic coupling leading to the population of *p* SAMO states could occur during the 20 fs pulse. Furthermore, the electric field of the pulse could also induce a dynamic Stark shift of the SAMO or Rydberg states that would decrease the energy gap between the SAMO and optically active valence states. The SAMO and Rydberg states could also be coupled to the optically active valence states but the transition dipole moment to these states is zero (see the transition dipole moments between the second band of active valence states and the *p*/*d*-SAMO in Fig. S2b). However, the transition dipole moments between the band of *p*-SAMO (that can be populated by vibronic coupling) and the *s*- and *d*-SAMO or Rydberg is very strong (Fig. S2c). This coupling can lead to population redistribution during the pulse. The band of *f*-Rydberg close to the IP cannot be accessed from *p*-SAMO states (due to symmetry reasons) but they are strongly coupled to *d*-SAMO states (Fig. S2c).

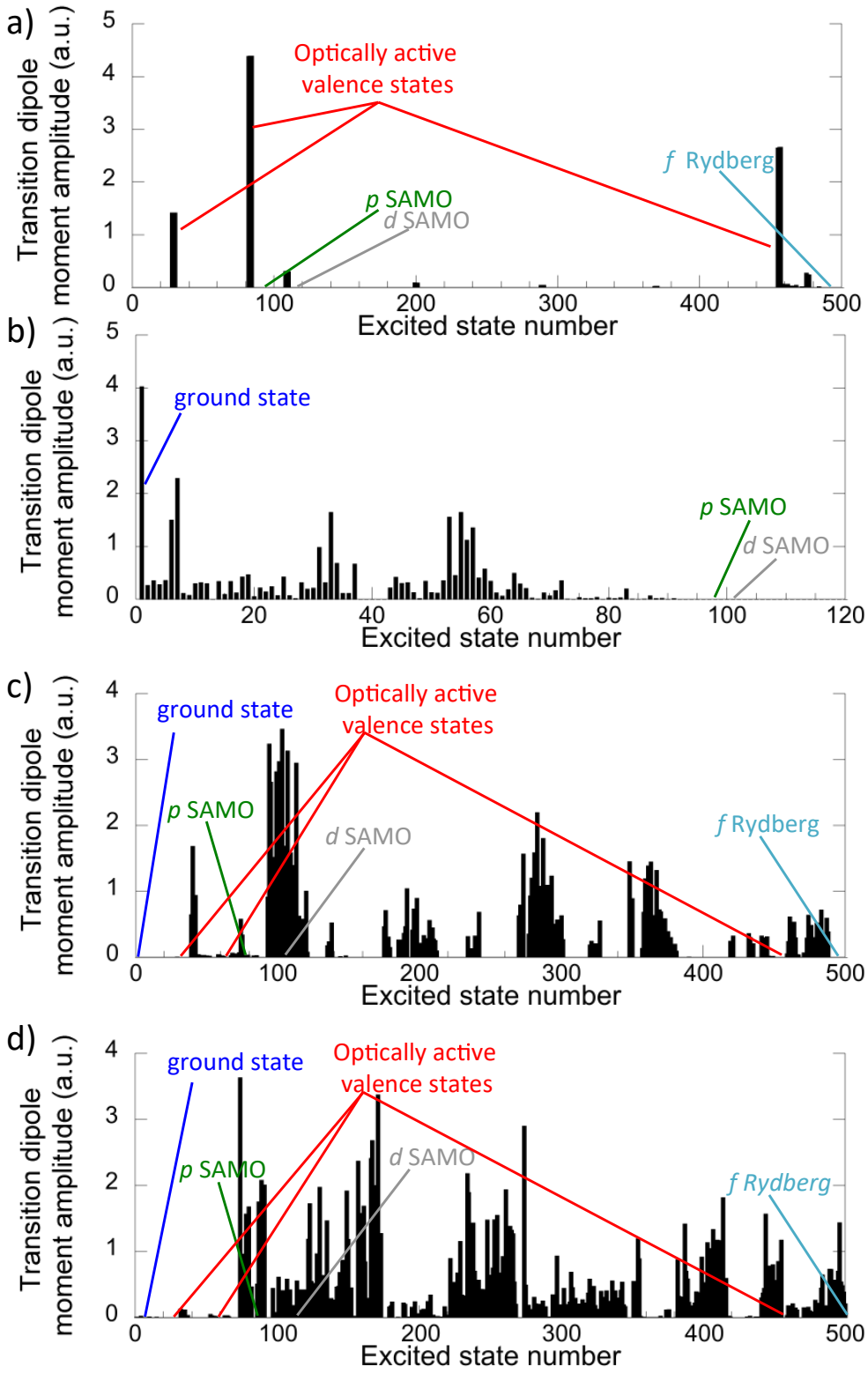

Fig. S2. Transition dipole moments between the ground state (a) and the 500 lowest excited states computed at the (LC-BLYP/6-31G(d) + set of 12 diffuse atomic orbitals) level. b) Transition dipole moments between the optically active valence excited state 82 (second band) and the 120 lowest excited states. c) Transition dipole moment between the *p*-SAMO and the 500 lowest excited states. d) Transition dipole moment between the *d*-SAMO and the 500 lowest excited states.

References

(1) Li, H. Study of Molecular Photoionization in Femtosecond Laser Fields. MSc thesis, Kansas-State University, 2013.

(2) Kling, N. G.; Paul, D.; Gura, A.; Laurent, G.; De, S.; Li, H.; Wang, Z.; Ahn, B.; Kim, C. H.; Kim, T. K.; Litvinyuk, I. V.; Cocke, C. L.; Ben-Itzhak, I.; Kim, D.; Kling, M. F., Thick-lens velocity-map imaging spectrometer with high resolution for high-energy charged particles. *J. Instrum.* **2014,** *9*, P05005.

(3) Vrakking, M. J. J., An iterative procedure for the inversion of two-dimensional ion/photoelectron imaging experiments. *Rev. Sci. Instrum.* **2001,** *72*, 4084-4089.

(4) Kling, M. F.; Rauschenberger, J.; Verhoef, A. J.; Hasović, E.; Uphues, T.; Milošević, D. B.; Muller, H. G.; Vrakking, M. J. J., Imaging of carrier-envelope phase effects in above-threshold ionization with intense few-cycle laser fields. *New J. Phys.* **2008,** *10*, 025024.