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### **Observation of ultrafast charge migration in an amino acid**

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Electron transfer within a single molecule is the fundamental step of many biological processes and chemical reactions. It plays a crucial role in catalysis, DNA damage, photosynthesis and photovoltaics. The investigation of this process has been the subject of considerable research effort [1]. Electron transfer driven by solely electronic correlations is well known as “charge migration” and it occurs in a few femtoseconds. In this work we present the first observation of ultrafast charge migration in the amino acid phenylalanine using XUV attosecond pulses. Neutral molecules were produced in gas phase by heating a thin metallic foil with a CW laser. Phenylalanine molecules were irradiated by a 250-as pump pulse with photon energy in the range 16-35 eV, followed by a 4-fs VIS/NIR probe pulse. The produced parent and fragment ions were then extracted into a linear TOF device for mass analysis. The main contributions in the mass spectrum correspond to the parent ion  $M^+$  (165 Da), the immonium ion ( $M-COOH = 120$ ), the backbone of the amino acid ( $M-R = 74$ ) and the phenyl groups ( $R = 91$ ,  $R + H = 92$ ). A small peak at 60 can be assigned to the doubly charged immonium ion [2]. Pump-probe measurements evidenced an exponential decay of the yield of fragment 60 with a time constant of 30 fs. This ultrashort time constant suggests that the dication dynamics is initiated by ionization of an inner-valence electron. By increasing the temporal resolution of the measurement we were able to observe a clear modulation of the yield with a periodicity of a few femtoseconds. This ultrafast dynamics can only be associated with purely electronic processes, thus constituting a clear experimental evidence of charge migration in biomolecules.

[1] O. Bixner et al., J. Chem. Phys. 136, 204503 (2012).

[2] L. Belshaw et al., J. Phys. Chem. Lett. 3, 3751 (2012).