Published in "The Journal of Physical Chemistry A 118(41): 9734–9744, 2014"
which should be cited to refer to this work.

Supporting Information

Joint experimental and theoretical study on vibrational excitation cross sections for electron collisions with diacetylene

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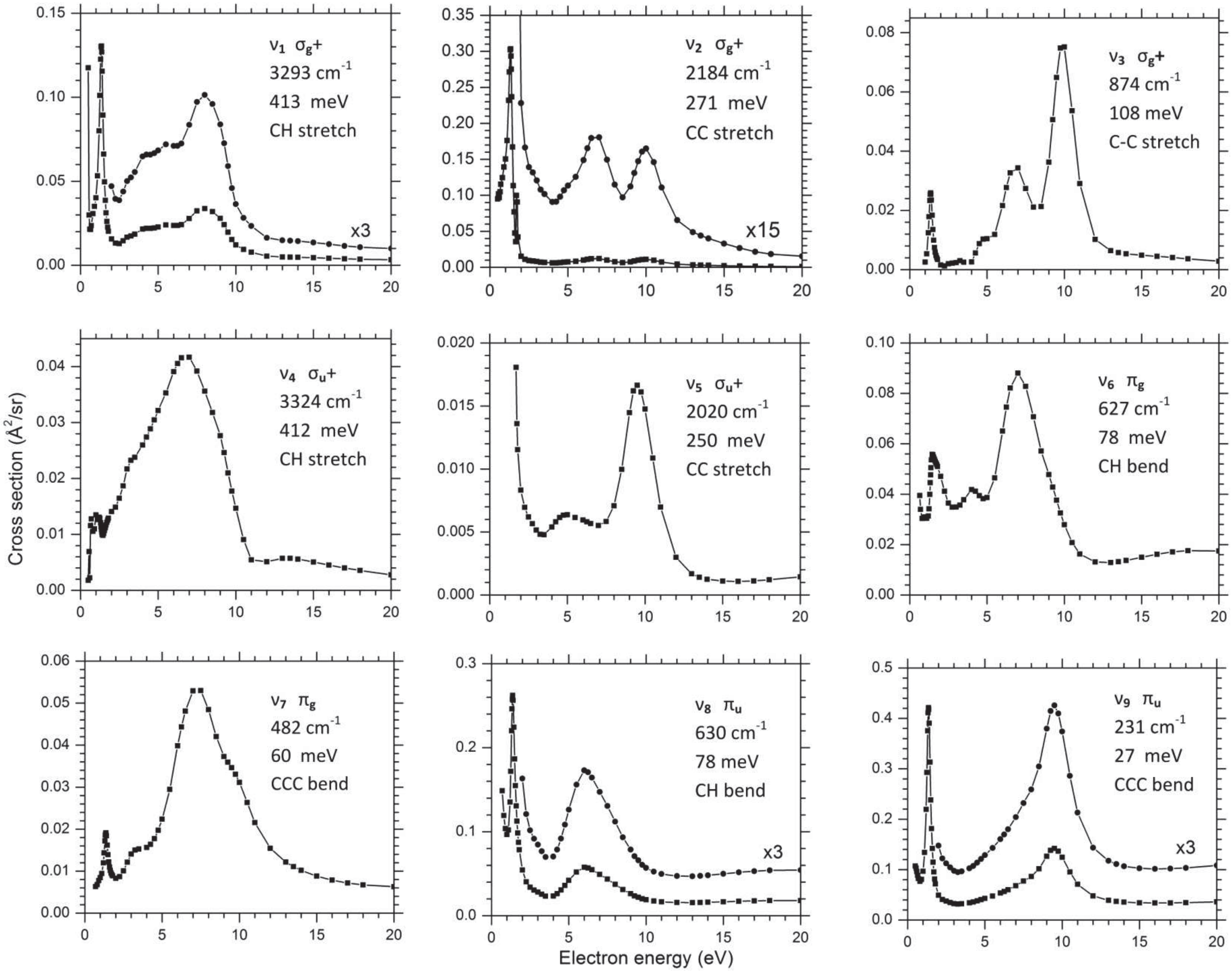
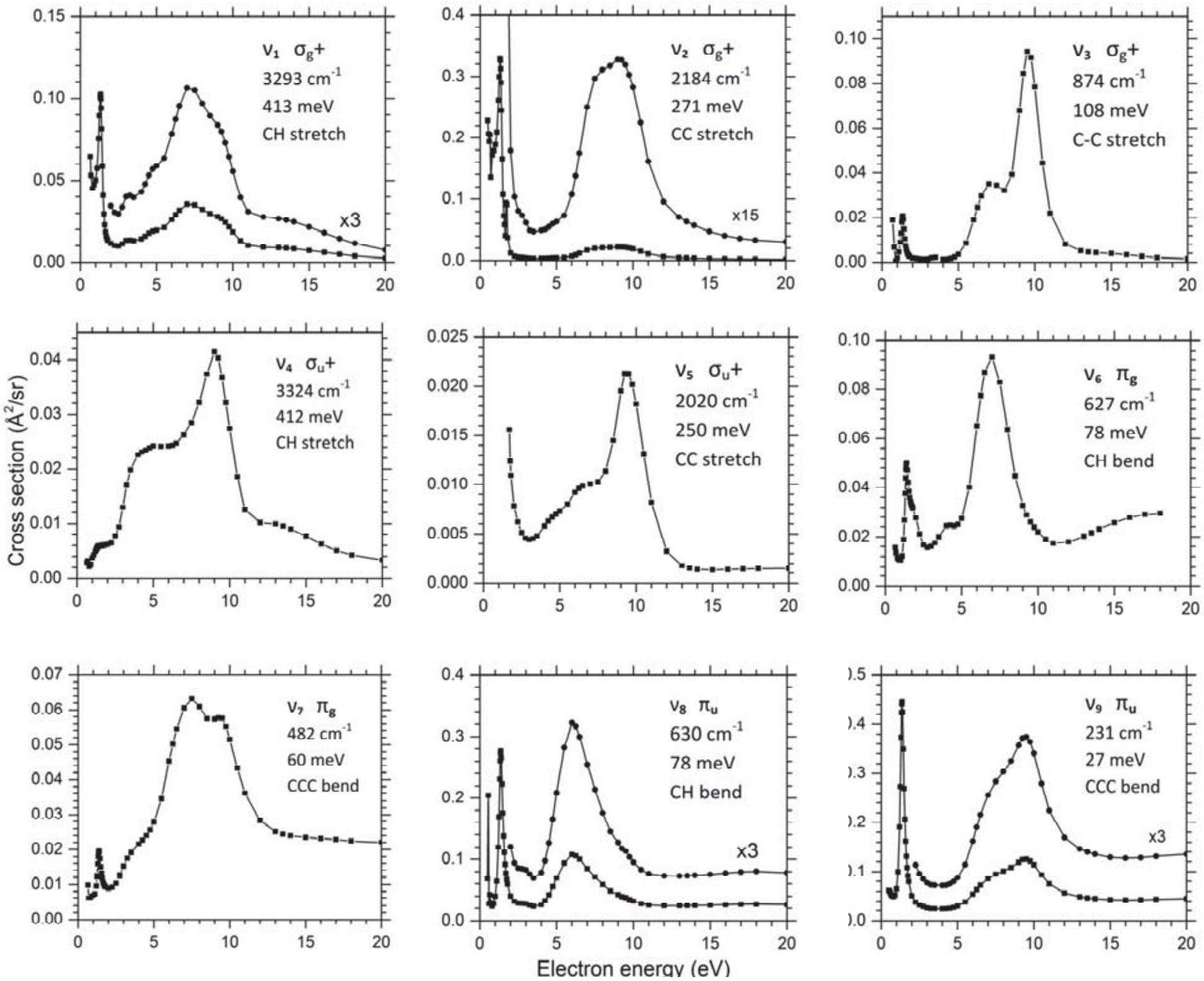
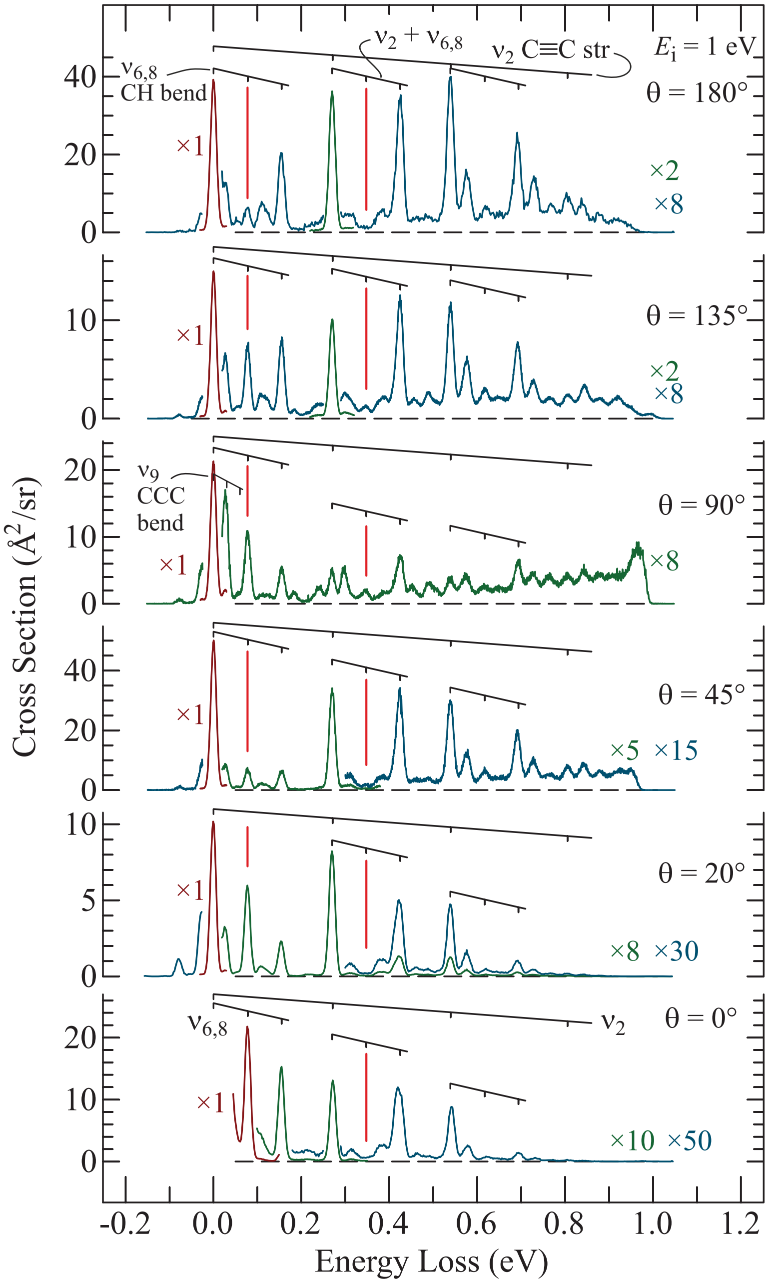


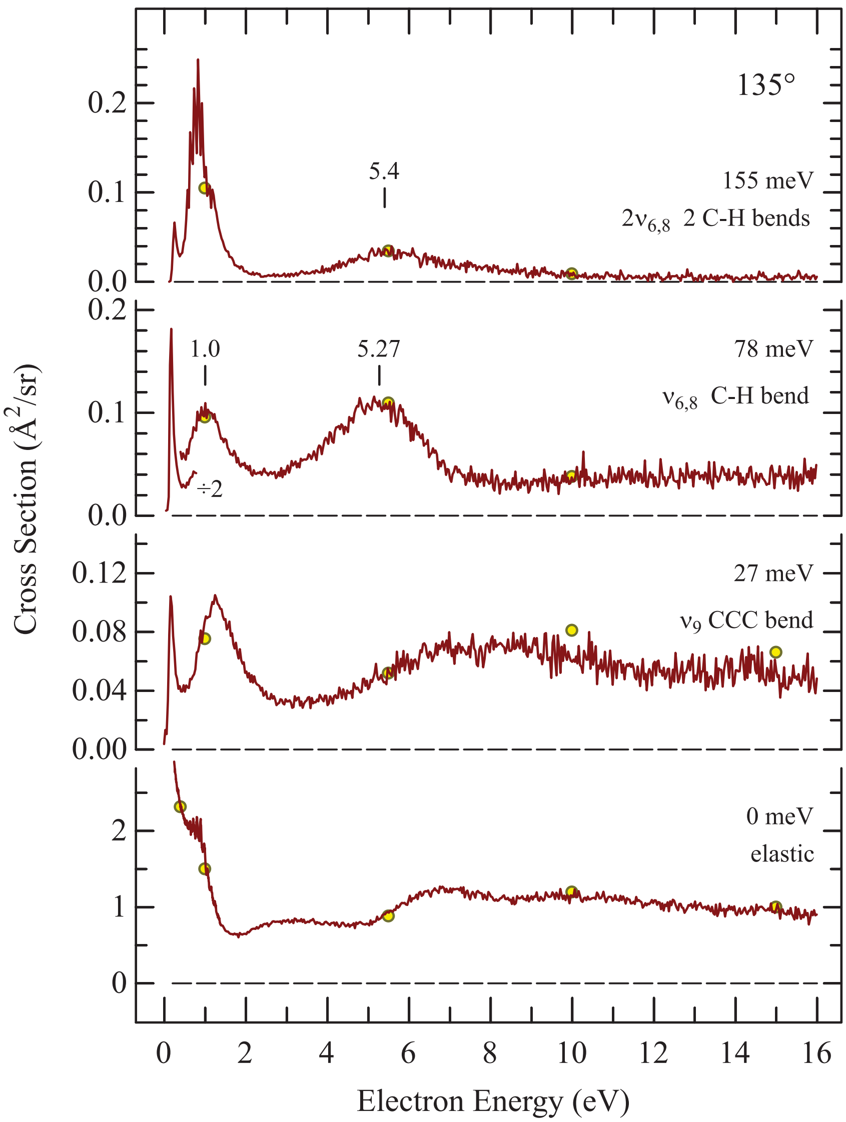
S1. Calculated energy dependences of vibrationally inelastic differential cross sections for nine normal modes of diacetylene at 45º.



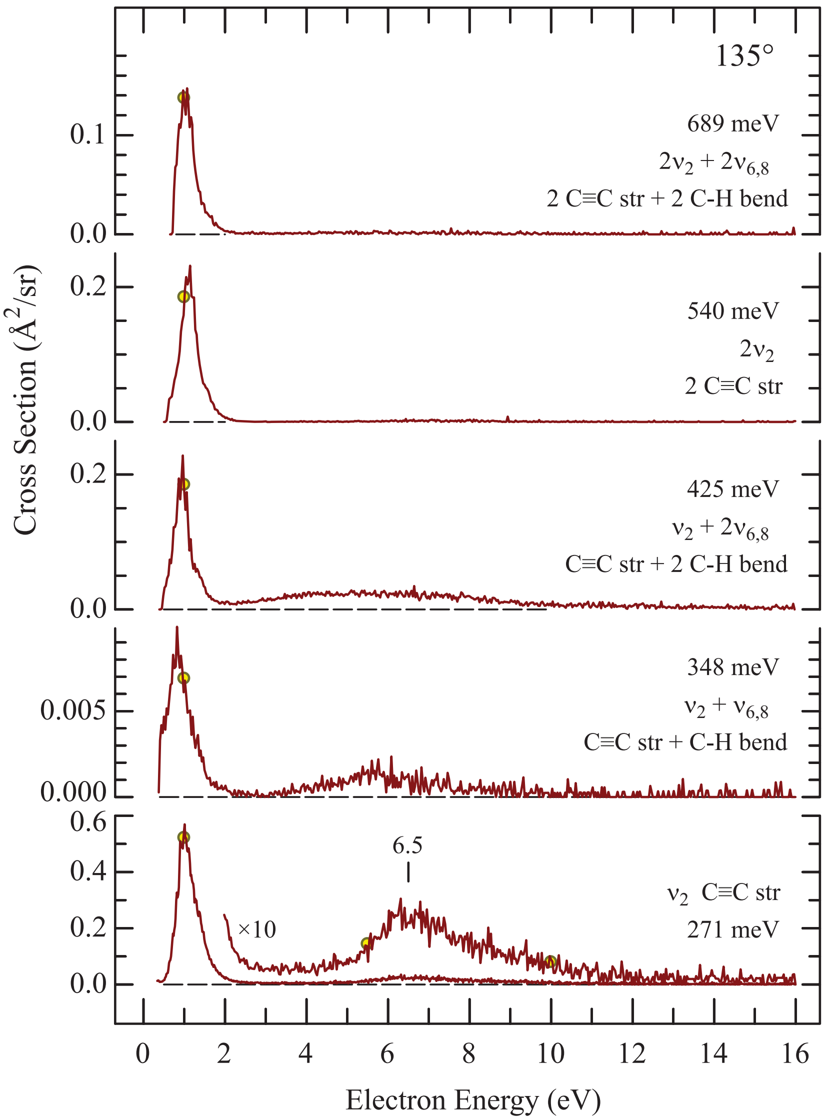
S2. Calculated energy dependences of vibrationally inelastic differential cross sections for nine normal modes of diacetylene at 135º.



S3. Overview of energy-loss spectra recorded at the incident energy of 1 eV, within the $^2\Pi_u$ resonance, at 6 different scattering angles. The spectra at 0°, 90° and 180° were already published in ref 1 and are reproduced here for a global comparison. The spectra illustrate the rich excitation of overtone and combination vibrations mentioned in the main text, which is due to the narrow autodetachment width of the $^2\Pi_u$ resonance. An interesting point is the increasing density of high overtones with low-frequency, observed at high energy losses (i.e., low scattered electron energies) and angles of 45° and higher. It is a manifestation of the 'unspecific' vibrational excitation, related to IVR. Another interesting point is the preference for exciting double quanta of the bending vibrations $\nu_{6,8}$, particularly clear in combination with ν_2, i.e., $\nu_2 + \nu_{6,8}$ is weak at 90° and 135° and practically missing at the other angles, whereas $\nu_2 + 2\nu_{6,8}$ is strong.[1]



S4. Overview of the cross sections recorded at 135°. The red lines are excitation functions; they are normalized to the individual absolute measurements, indicated by yellow circles. The curves recorded at energy-losses of ΔE = 27 meV and ΔE = 78 meV have threshold peaks, presumably a consequence of the IR activity of the ν_9 (weak) and ν_8 (strong) normal modes. The cross section for the overtone at ΔE = 155 meV, only weakly IR active, has only a weak threshold peak. Note that the $^2\Pi_u$ resonance at 1 eV has a deep boomerang structure in the overtone excitation at ΔE = 155 meV, but no boomerang structure in the excitation of the fundamental at ΔE = 78 meV. This reflects the entirely different excitation mechanism, revealed also by the dramatically different angular distributions.[1] The $^2\Pi_g$ resonance at 5.3 eV is much weaker, relatively to the $^2\Pi_u$ resonance at 1 eV, in the overtone excitation than in the fundamental excitation, reflecting its much larger autodetachment width. This is already indicated by the absence of boomerang structure.



S5. Continuation of S4, for higher-lying vibrational states. Note that the 6.5 eV resonance excites overtones such as $2\nu_2$ more weakly than the longer-lived 1.0 eV resonance. The stronger excitation of double quanta of $2\nu_{6,8}$ is also seen.

1. M. Allan, O. May, J. Fedor, B. C. Ibănescu and L. Andric, *Phys. Rev. A* **2011,** 83, 052701.