Comment on "Dipole-Supported Electronic Resonances Mediate Electron-Induced Amide Bond Cleavage"

Recently, Li *et al.* [1] reported cleavage of the amide bond in formamide, *N*-methylformamide (NMF), and *N*, *N*-dimethylformamide (DMF) via dissociative electron attachment (DEA). They concluded that the lowest DEA band is mediated by a novel type of electronic resonance, a dipole-supported core-excited resonance. There were two main arguments for this conclusion: (i) elimination of other common types of resonances and (ii) coincidence of the DEA bands with the calculated highly polar excited states of the neutral. I suggest that one of the mechanisms that was eliminated by Li *et al.*, and which is common in organic molecules, is operative also in the molecules in question.

At issue are the Feshbach resonances with two electrons occupying Rydberg orbitals. Li *et al.* estimated the lowest energy of such configuration in formamide to be 6.5 eV and thus concluded that it cannot be responsible for their DEA band at 5.9 eV. This estimate was obtained using the empirical relation of Spence [2], placing such resonance 3.9 eV below the lowest ionization potential (IP). However, later systematic studies [3–5] showed that the difference between the IP and DEA bands varies between 2.5 and 4.6 eV, with the majority of molecules lying in the upper part of this range. The 4.42 eV difference in formamide ($\mathrm{IP} = 10.32$ eV) [6] is thus in the common range. There are several facts that suggest the assignment of the formamide 5.9 eV DEA band to an s^2-type Feshbach resonance.

(i) Gingell *et al.* [7] measured excited states of neutral formamide using VUV spectroscopy [Fig. 1(b)]. The lowest Rydberg state (R_1) was identified at 6.35 eV and corresponds to the $n_\mathrm{O}3s$ or $\pi_2 3s$ configurations (nearly degenerate). The 5.9 eV DEA band is 0.45 eV lower in energy, which is a common estimate for the stabilization energy of the s^2 Rydberg pair [2,4].

(ii) Li *et al.* reported that this DEA band shifts to lower energies in the series formamide, NMF, and DMF, as 5.9, 5.5, and 5.4 eV, respectively. The corresponding lowest IPs are 10.32, 9.87, and 9.27 eV [6]. This supports the assignment of the lowest cation ground state as the grandparent state of the Feshbach resonance.

(iii) If the Feshbach resonance associated with the lowest IP leads to DEA, one can expect the same for the resonances associated with higher IPs. Assuming a constant shift, the $9a'3s^2$ resonance ($\mathrm{IP} = 14.2$ eV) [6] should be at approximately 9.8 eV and the $8a'3s^2$ resonance should be at around 11.9 eV ($\mathrm{IP} = 16.3$ eV) [6]. Indeed, such bands do occur in the DEA of formamide [8], and they decay into O^- and NH^- fragments.

Li *et al.* attributed the formamide 5.9 eV DEA band to the dipole-supported resonance correlating with ${}^3\pi\pi^*$ state of the neutral. Gingell *et al.* [7] characterized also triplet states [Fig. 1(c)]. Contrary to low-dipole triplets ${}^3n_\mathrm{O}\pi^*$ (5.2 eV) and ${}^3n_\mathrm{O}3s/{}^3n_\mathrm{O}\pi$ (6–7 eV), the high-dipole ${}^3\pi\pi^*$ state is invisible in the spectrum. There might be a weak footprint of it around 5.7 eV, manifested by the shift of the minimum between the main triplet bands [7]. In any case, the electron-induced excitation of this high-dipole triplet state is inefficient. The dipole-supported resonances could contribute to the higher lying DEA bands, together with similar core-excited mechanisms suggested earlier [9,10].

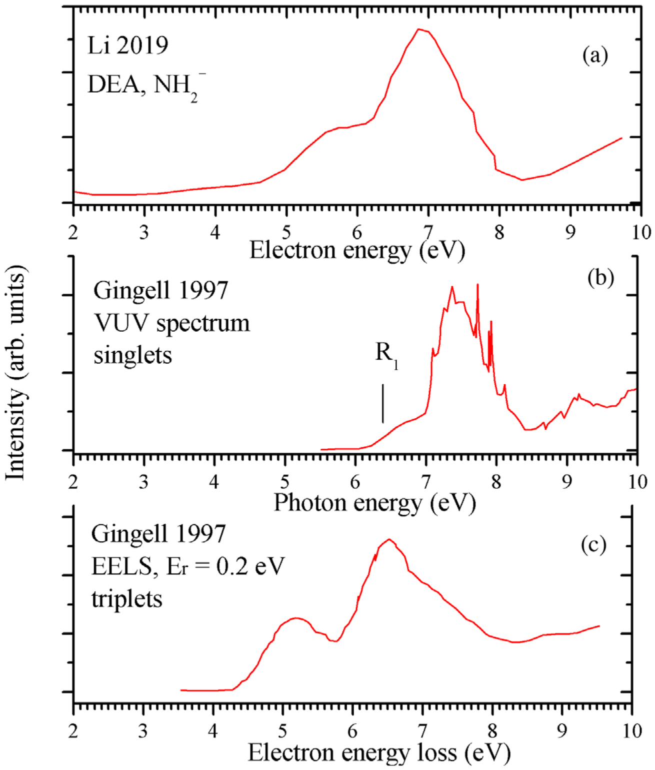

FIG. 1. (a) DEA spectrum [1], (b) VUV spectrum [7], and (c) near-threshold electron energy loss spectrum [7] (EELS) of formamide.

J. Fedor
J. Heyrovský Institute of Physical Chemistry
Czech Academy of Sciences
Dolejškova 3, 18223 Prague, Czech Republic

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