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Comment on “Radiation damage of biosystems mediated by secondary electrons: Resonant precursors for uracil molecules” †[*J. Chem. Phys.* 120, 7446 (2004)]

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# Comment on “Radiation damage of biosystems mediated by secondary electrons: Resonant precursors for uracil molecules”

## [J. Chem. Phys. 120, 7446 (2004)]

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Gianturco and Lucchese<sup>1</sup> have recently presented calculations reporting resonances in the electron scattering cross section of the RNA base uracil and discussed the role of these temporary negative ion states in various fragmentation processes. Such efforts in complex systems are highly commendable. However, the authors have not made a proper comparison of their calculated anion states with those measured and assigned earlier,<sup>2</sup> although this latter work is cited in their paper. In particular, they omit any reference to the lowest-lying resonance observed previously.

Of the five single-particle resonances discussed in Ref. 1, three have  $\pi$  symmetry and, in the simplest picture, will correspond to electron attachment into the three molecular orbitals made up of combinations of the antibonding  $\pi^*$  orbitals of the C=C and the two C=O groups of uracil. Resonances in uracil have been studied previously<sup>2</sup> by electron transmission spectroscopy (ETS).<sup>3</sup> Three prominent features were observed in the total scattering cross section, lying at 0.22, 1.58, and 3.83 eV. (A more recent measurement<sup>4</sup> places the lowest feature at 0.27 eV.) The resonances were assigned to the three empty  $\pi^*$  orbitals by the use of calculated virtual orbital energies (VOEs). It is well known that the VOEs given by an electronic structure calculation of a neutral molecule, using an appropriately sized basis set, may be associated with the valence negative ion states of the molecule through Koopmans' theorem.<sup>5</sup> It is also known that such energies are in error in an absolute sense, for reasons that are well understood.<sup>6</sup> However, plots of calculated VOEs as a function of measured resonance energies in unsaturated molecules show very good correlations<sup>6,7</sup> for the low-lying  $\pi^*$  resonances. In other words, by shifting and scaling the VOEs semiempirically, one may use this correlation to predict resonance energies in other compounds. Not surprisingly, the closer the structures of the molecules in the correlation plot are to those being studied, the better the predictive ability. Such calculations have been routinely carried out for unsaturated compounds in many chemical families.<sup>8</sup> This approach is particularly useful and most accurate in locating the lowest lying, and generally longest lived,  $\pi^*$  anion state in a given compound. Scalings determined from other reference molecules will, of course, differ, but typically there is agreement better than 0.2 eV. The correlation tends to be less accurate for higher-lying  $\pi^*$  anion states.

From their calculations Gianturco and Lucchese predict three resonances of  $\pi$  symmetry and report their energies as 2.27, 3.51, and 6.50 eV. The “wave function maps” of these resonances are shown in Figs. 7 and 8 of their paper. We point out that these plots match in every significant detail with the orbitals computed from the structure calculations referred to above (plotted but not published in Ref. 2). Thus there is no doubt that the resonances predicted in the scattering calculations correspond to electron attachment into the  $\pi_1^*$ ,  $\pi_2^*$ , and  $\pi_3^*$  orbitals, respectively. Because of approximations made in the scattering calculations, the authors state that it is not expected that the resonance energies will agree precisely with experiment. However, they continue by suggesting approximate agreement of their *lower* two  $\pi^*$  resonances with the *upper* two determined by ETS. No justification is presented for the absence of the lowest state determined by ETS in this comparison. In fact, a uniform downward shift of 2 eV in the resonances computed by Gianturco and Lucchese gives excellent agreement with the lowest two  $\pi^*$  anion states found by ETS, and the third anion state would lie only about 0.7 eV above experiment.

Needless to say, the precise energies and assignments are important for a meaningful discussion of the fragmentation processes. If the calculated 6.5 eV resonance actually lies at 3.83 eV as given by ETS, then its involvement in the reactions in the 6.5–7 eV range discussed in Ref. 1 is not possible. The source for these latter processes is clearly through core-excited resonances, which are not included in the theoretical treatment.

Gianturco and Lucchese also report two resonances of  $\sigma$  symmetry at 0.012 and 10.73 eV. Given the errors in the computed  $\pi^*$  resonances energies, these values are problematic. The lower  $\sigma^*$  resonance, shown in Fig. 5 of Ref. 1, has some but not all of the characteristics of the lowest (valence) virtual orbital of  $\sigma$  symmetry, consequently it is not clear that it can be so identified. Our scaling procedure places the lowest  $\sigma^*$  resonance above 2 eV.

Noting that a realistic treatment of the dissociative attachment process in such complex molecules is still out of reach, the authors attempt, by considering the wave functions of the two  $\sigma^*$  resonances, to determine the suitability of these resonances as precursors of the specific dissociative paths observed experimentally. In the case of the lower  $\sigma^*$  resonance, the low electron density at the N<sub>3</sub>–H bond is sug-

gested to lead to the ejection of this H atom, leaving the additional electron on the molecular frame. This is quite counter to chemical intuition. In fact, it is the N<sub>1</sub>-H bond that is broken, in part a consequence of the *strongly antibonding* character of the lowest  $\sigma^*$  orbital at this site. A more complete discussion of this resonance, the dipole bond anion state, and their roles in the dissociative attachment process may be found elsewhere.<sup>4</sup>

The amplitudes and nodal characteristics of the resonance orbitals (at the geometry of the neutral molecule) certainly give clues to the impulses delivered to the nuclei during the lifetimes of the resonances. In the absence of bond strengths, electron affinities of the fragments and the poten-

tial surface gradients, however, these properties alone are not sufficient to predict the products.

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<sup>6</sup>See, for example, D. Chen and G. A. Gallup, J. Chem. Phys. **93**, 8893 (1990).

<sup>7</sup>S. W. Staley and J. T. Strnad, J. Phys. Chem. **98**, 116 (1994).

<sup>8</sup>A bibliography of ETS papers may be found at [www.physics.unl.edu/directory/burrow/Files/ETS2002.PDF](http://www.physics.unl.edu/directory/burrow/Files/ETS2002.PDF)