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Comment on the negative ion states of fluorobenzenes

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In a recent paper Frazier *et al.*[1] reported a study employing electron transmission spectroscopy (ETS) to determine the energies of the temporary negative ion states associated with the occupation of the three low-lying π^* orbitals of benzene and several fluorobenzenes. The purpose of the present note is to point out that the theoretical model used by Frazier *et al.*[1] to account for the substituent effects is inadequate, and in particular does not yield the proper symmetry assignments of the first two anion and cation states of fluorobenzene and *p*-difluorobenzene.

In the model of Frazier *et al.* the anion and cation states are stabilized upon fluorine substitution by an amount $\sum_{i=j} |c_i|^2\gamma$, where the $\{c_i\}$ are the coefficients of the π orbitals of benzene, as given in a Hückel picture, and the sum runs over those atoms (denoted by "*j*") to which fluorines are attached. The parameter γ was chosen to provide the best fit to the anion and cation energies. While this model *appeared* to work well for fluorobenzene, *p*-difluorobenzene, and 1, 3, 5-trifluorobenzene, it was in error by 0.2–0.6 eV for the first two anion states of 1, 2, 4, 5-tetrafluorobenzene, penta- and hexafluorobenzene.

The reason for the inability of this model to predict accurately the energies of the temporary anions of these last three molecules is that it allows for only a stabilizing interaction by fluorine. It is well known[2] that fluorine exerts both a stabilizing inductive and destabilizing resonance effect on the π orbitals of unsaturated hydrocarbons.

A simple model incorporating both effects through an expression of the form $\{\sum_{i=j} |c_i|^2 X + \sum_{i=j\pm1} |c_i|^2 I^{NN}\}$ is able to predict the first two π EA's and IP's of these compounds to greater accuracy. In this expression $X = R + I^A$, where R is the resonance contribution and I^A is the inductive contribution of a fluorine at the carbon to which it is attached. I^{NN} denotes the inductive effect at the nearest neighbor carbon atoms. The choice $X = 0.56$ eV, $I^{NN} = -0.70$ eV gives the first two IP's and EA's of these compounds to within 0.3 eV of their experimental values. Considerably better results are obtained if different parameters are utilized for the anion and cation states. The choice $X = 0.60$ eV and $I^{NN} = -0.60$ eV works quite well for the EA's, while $X = 0.52$ eV and $I^{NN} = -0.80$ eV gives a good description of the IP's.

A two-parameter fit should, of course, yield more accurate results than can be obtained with a single parameter. However, by accounting properly for the two substituent effects, we find also a difference in the predicted symmetry assignments for certain of the molecules. The degenerate, unoccupied π^* orbital of benzene is split upon substitution yielding a_2 and b_1 orbitals in the C_{2v} point group and b_{3u} and a_u orbitals in the D_{2h} point group. While the model of Frazier *et al.* predicts that the lowest π-type anion of fluoro and *p*-difluorobenzene is B_1 and B_{3u}, respectively, the model including both resonance and inductive effects yields A_2 and A_u, respectively. Additional support for our symmetry assignment is provided by *ab initio* calculations[3] and by EPR studies in matrices.[4]

We note also that the ordering of the first two IP's of fluorobenzene and *p*-difluorobenzene as predicted by the model of Frazier *et al.* is not in agreement with the assignments as determined by the angular distributions of the photoionized electrons.[5]

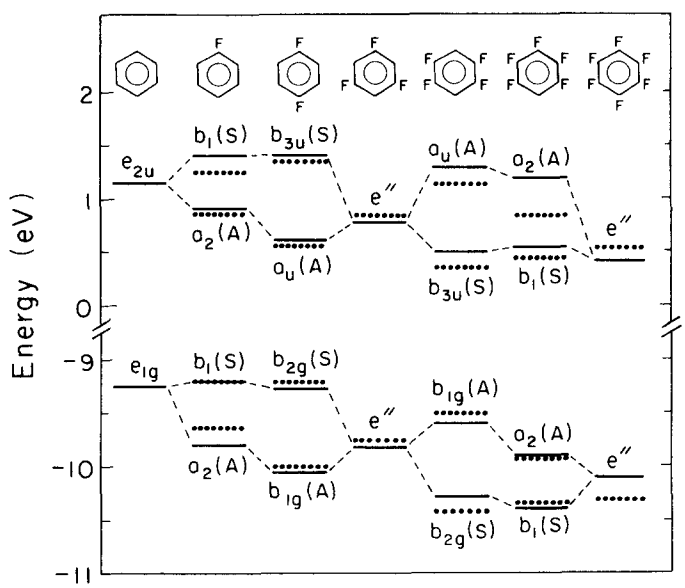

FIG. 1. Correlation diagram for the vertical EA's and IP's of benzene and various fluoro-substituted benzenes. The solid lines refer to the experimental values and the dots to the values obtained from the two-parameter induction-resonance model described in the text. The experimental IP's for 1, 2, 4, 5-tetrafluorobenzene and penta-fluorobenzene are from Ref. 1, while those for the other compounds are from Ref. 5. The orbitals are labeled S or A, depending on whether they are symmetric or antisymmetric under reflection in the plane passing through the C_1 and C_4 carbons, perpendicular to the plane of the ring.

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In Fig. 1, we present a correlation diagram of the calculated and experimental EA's and IP's derived from the degenerate e_{2u} and e_{1g} benzene orbitals, respectively. The overall agreement for the third π^* anion state is much poorer and is not improved over that calculated by Frazier *et al.* In part, the reason for this may be that the third anion state is not as well described by a single configurational wavefunction.

We have plotted the experimental vertical EA's as listed by Frazier *et al.*[1] except for benzene which we believe to be in substantial error. The criterion used by these authors to justify a vertical EA of -1.35 eV was not discussed. For anions which are sufficiently long-lived to display well-defined vibrational structure, the vertical EA's should be determined from the most intense member of the vibrational progression. For the ground state (E_{2u}) anion of benzene the lowest member is clearly the strongest. A vertical EA of -1.15 ± 0.03 eV has previously been determined for benzene by Burrow *et al.*[3] Our interpretation of the data of Frazier *et al.* yields vertical EA's for certain of the other compounds, in particular, 1, 2, 4, 5-tetrafluorobenzene and pentafluorobenzene which differ somewhat from the values assigned by these authors. The reinterpreted values are in better agreement with the predictions of the model described in this note and with our own measurements.[6]

Finally, we observe that the model employed by Frazier *et al.* was employed earlier by Christophorou *et al.*[7] in their assignments of the anion states of several monosubstituted benzenes. In view of the above discussion, we believe that the assignments given in that paper should be reconsidered. In particular we note that their assignments of the anion states of aniline, phenol, and anisole differ from those presented in Ref. 3.

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Comment in reply to K. D. Jordan and P. D. Burrow's "Comment on the negative ion states of fluorobenzenes"

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The theoretical treatment of Frazier *et al.*[1] gave good predictions of the energy positions of the observed π-negative ion states in substituted fluorobenzenes using only one disposable parameter. The treatment of K. D. Jordan and P. D. Burrow in the preceding comment uses two or four parameters; it can be reduced mathematically to the form of Frazier *et al.* plus a small or zero correction and, in our opinion, provides only a marginal improvement over our simple first-order perturbation treatment for the energies.

We believe that neither our nor Jordan and Burrow's treatment is adequate to fully describe the negative ion states of benzene and its derivatives and their symmetry assignments. The latter will be unambiguously determined from truly *ab initio* calculations and/or from further experimental work on the angular distribution of electrons scattered indirectly via these negative ion states. The experimental work[2,3] they refer to cannot provide unambiguous assignments since the EPR studies quoted[2] were performed in the condensed phase where relaxation processes and medium effects influence the anionic states, and the PES work they cite[3] merely identifies the states under consideration as π states (and we all agree on that!); it provides no unambiguous information (the values of the asymmetry parameter for the b_1 and a_2 orbitals are within the quoted experimental errors)[3] for symmetry assignments.

In the absence of such calculations or experiments, we adduced support for our symmetry assignment of the lowest unoccupied π orbital in fluorobenzene from electron swarm-beam experiments[4] on the production of Cl^- from C_6H_5Cl via dissociative attachment and from electron transmission[5] and threshold-electron excitation[6] experiments. The former[4] located the maximum of the Cl^-/C_6H_5Cl resonance at 0.86 eV and the latter[5,6] located the lowest negative ion resonance of C_6H_5Cl at

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