to emitter as length, amount, density, and morphology of the cobalt dendrites vary slightly.

The influence of an electric field gradient on the position of chemical equilibrium has been treated by several workers.[14–16] Application of an appropriate model[14] to this example adequately predicts the protonation of molecules of low basicity by carboxylic acids in a strong electric field in our observations; this will be amplified in the full paper.

We propose the study of the attachment of surface groups to other kinds[17–20] of field desorption emitters. Goals of such work could be the protection of the sample against decomposition by native surface groups, and altering spectra in a predictable manner, as we have demonstrated here.

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Temporary Negative Ions of Methyl-Substituted Ethylenes: Trends in the Electron Affinities, Ionization Potentials, and Excitation Energies

Sir:

Many investigations have addressed the effect of alkyl groups on various properties of unsaturated hydrocarbons. Although the π ionization potentials and the $\pi \rightarrow \pi^*$ excitation energies are known for the methyl-substituted ethylenes, a complete set of accurate electron affinities (EA) is not available. To this end, we have employed electron transmission spectroscopy (ETS)[1,2] to study the ground-state negative ions of the methyl-substituted ethylenes. We then combine the resulting electron affinities with existing ionization potential (IP) data to explore the relationship between the lowest singlet and triplet $\pi \rightarrow \pi^*$ excitation energies and the quantity IP − EA. A similar investigation[3] carried out on the fluoroethylenes revealed an approximately linear dependence of the triplet energies on IP − EA. For the singlet state, only the symmetrically substituted compounds displayed this behavior, with the asymmetrically substituted compounds falling well below the line. If this behavior is indeed the result of symmetry differences, similar trends would be expected upon methyl substitution even though methyl groups and fluorine atoms have very different inductive and mesomeric properties.

Using ETS, one can determine the energies of anion states lying above the ground state of the neutral molecule from the positions of resonances, i.e., rapidly varying structures, in the electron-scattering cross section. The electron transmission spectra of ethylene and the methyl-substituted ethylenes are presented in Figure 1. The structure which occurs in the 1–2-eV region of the ethylene spectrum has been assigned[4] to the temporary anion formed by the capture of an electron into the b_{2g} (π^*) orbital. The corresponding features in the spectra of the methyl derivatives, which are only slightly shifted from that of ethylene, can likewise be associated with the capture of electrons into the low-lying π^* orbitals. The vertical EAs determined from the transmission spectra are summarized along with the IPs and the neutral excitation energies in Table I. Electron affinities obtained by other workers with the trapped electron method (TEM)[5] are also listed.

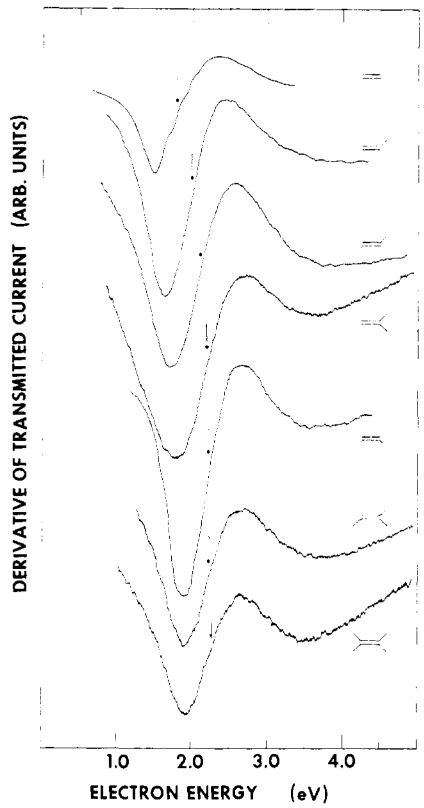

Figure 1. The derivative with respect to energy of electron current transmitted through ethylene and the methyl-substituted ethylenes as a function of impact energy. The arrows indicate the midpoints between the extrema of the derivative. These energies are taken as the vertical attachment energies, that is, the negatives of the vertical electron affinities. Faint undulations in the lower curves are due to a N_2 impurity.

Table I. Vertical Ionization Potentials, Electron Affinities, and Rydberg, Singlet, and Triplet Transition Energies (eV)

compd	IP[a]	EA[b] (ETS)	EA[c] (TEM)	EA[d] (TEM)	T[e]	S[f]	R[f]
ethylene	10.515	−1.78	−1.87	−1.8	4.32	7.58	7.15
propene	9.744	−1.99	−2.2		4.28	7.15	6.72
isobutylene	9.239	−2.19			4.22	6.68	6.19
cis-2-butene	9.124	−2.22	−2.3	−2.3	4.21	7.10	6.03
trans-2-butene	9.122	−2.10	−2.4	−2.2	4.24	6.97	6.09
trimethyl-ethylene	8.682	−2.24			4.16	6.75	5.74
tetramethyl-ethylene	8.271	−2.27		−2.0	4.10	6.61	5.40

[a] Reference 9. [b] This study. [c] Reference 13. [d] Reference 14. [e] Reference 11. [f] Reference 12.

The weak undulations appearing in the ethylene spectrum have been assigned[6] to ν_2, the C–C stretching mode. Fine structure due to nuclear motion is not seen in the transmission spectra of the substituted ethylenes. This indicates that methyl substitution

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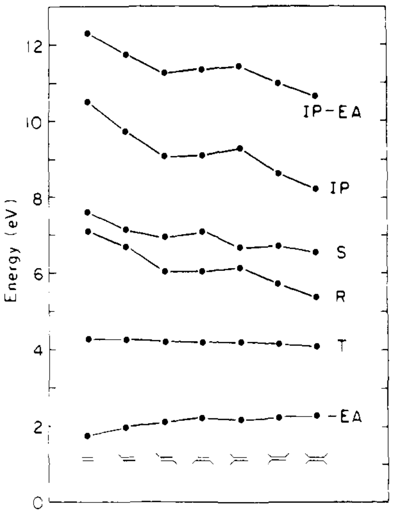

Figure 2. Correlation diagram of the experimental EAs, IPs, IP − EA, lowest Rydberg (R), and singlet (S) and triplet (T) π → π* excitation energies.

causes a decrease in the lifetime of the anion. A similar effect has also been observed in benzene[7] and formaldehyde.[8]

With the exception of *cis*-2-butene, each additional methyl group causes a small change in the EA; the largest shift (0.21 eV) occurs between ethylene and propene. Furthermore, the shifts in the EAs are substantially smaller than those in the IPs.[9] These qualitative trends are consistent with the hyperconjugation model,[10] which focuses on the interaction between the methyl group orbitals of π symmetry, denoted π_{CH_3} and $\pi_{CH_3}{}^*$, and the π_{CC} and the $\pi_{CC}{}^*$ orbitals of ethylene. The energy separations are such that the π_{CC} orbital is expected to be significantly destabilized by the π_{CH_3} orbital and essentially unperturbed by the $\pi_{CH_3}{}^*$ orbital. On the other hand, the $\pi_{CC}{}^*$ orbital is destabilized by the π_{CH_3} and stabilized by the $\pi_{CH_3}{}^*$ orbitals. The ETS results indicate that the former interaction dominates. In this picture, shifts in the π* orbital energy are predicted to be much smaller than those for the π, and each additional methyl should cause a smaller shift in the IP and EA.

The first Rydberg,[11] the π → π* singlet,[11] and triplet[12] excitation energies, together with the IPs, EAs, and IP − EAs, are presented in Figure 2. As expected, the Rydberg transition energies parallel the IPs. The situation for the π → π* energies is more complicated. The effect of methyl subsitution on the singlet transition energies is appreciable but does not simply parallel that in the IPs. On the other hand, there is little variation in the triplet excitation energies. Formally, one can express the excitation energies in terms of the quantity IP − EA plus a sum of two electron interaction terms.[15] Since simple relationships have been found between the experimental excitation energies and the IP − EAs of other compounds,[2,3] we also explore this possibility for the methylethylenes.

In Figure 3, the singlet (S) and triplet (T) energies are plotted vs. IP − EA. For the triplets, a straight line fits the results to better than 0.05 eV. Similar behavior was found for the fluoroethylenes,[3] even though the effect of fluorine substitution on the IPs and EAs is markedly different.

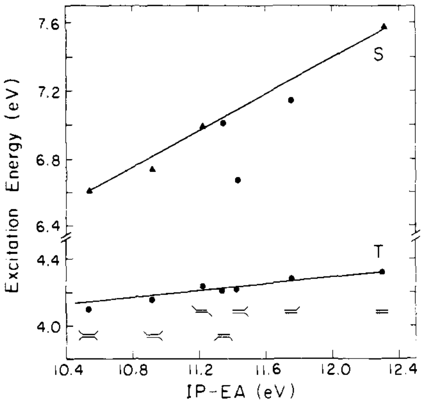

Figure 3. Singlet (S) and triplet (T) excitation energies vs. IP − EA.

A good fit is obtained for the singlet states of the methylethylenes only if the asymmetrically substituted compounds propene, isobutylene, and trimethylethylene are excluded. A similar result was found for the fluoroethylenes, although the deviation of the asymmetrically substituted compounds from the line was more pronounced, ranging from 0.3 eV for fluoroethylene to 0.9 eV for 1,1-difluoroethylene as compared to 0.1–0.4 eV for the methylethylenes. Again, the greatest effect is in the 1,1-disubstituted compound. We estimate that the *relative* values for the vertical EAs, IPs, and excitation energies are accurate to better than 0.05 eV. Hence, the deviations of the singlet transition energies of the asymmetrically substituted compounds are significant. The methylethylene results support our contention that the key to the effect is the molecular symmetry rather than the nature of the substituent. In the symmetrical species, the π → π* singlet is of different symmetry than the $\pi^2 \rightarrow (\pi^*)^2$ doubly excited singlet; hence, they cannot mix. In the asymmetrically substituted compounds, the symmetry lowering permits these configurations to mix, causing a decrease in the π → π* singlet energies.

In principle, it should be possible to confirm this picture by using ab initio self-consistent field configuration interaction calculations. However, it is well-known that an accurate theoretical description of the singlet excited state of ethylene alone requires large basis sets and extensive configuration mixing,[16] making similar calculations on the substituted ethylenes costly. Some additional support for our view of the role of configuration mixing is provided by ab initio calculations at the single configuration level. Such calculations yield a nearly linear dependence between both the singlet and the triplet π → π* excitation energies and IP − EAs for the fluoroethylenes, in contrast with experiment.

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