PHYSICAL REVIEW B VOLUME 30, NUMBER 1 1 JULY 1984

Brief Reports

Brief Reports are short papers which report on completed research which, while meeting the usual **Physical Review** *standards of scientific quality, does not warrant a regular article. (Addenda to papers previously published in the* **Physical Review** *by the same authors are included in Brief Reports.) A Brief Report may be no longer than 3½ printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Electron-stimulated desorption from partially fluorinated hydrocarbon thin films: Molecules with common versus separate hydrogen and fluorine bonding sites

J. A. Kelber and M. L. Knotek
Sandia National Laboratories, Albuquerque, New Mexico 87185

(Received 1 February 1984)

We have observed H^+ and F^+ yields as a function of low-energy (10–100 eV) electron bombardment from thin films of solid nonafluoroisobutane [$(CF_3)_3CH$], 1,2,3,5-tetrafluorobenzene ($C_6H_2F_4$), 1-fluorobutane (C_4H_9F), and fluorocyclohexane ($C_6H_{11}F$). For the materials with separate H and F bonding sites [$C_6H_2F_4$ and $(CF_3)_3CH$], H^+ and F^+ have different appearance potentials, corresponding, respectively, to excitations of the C 2*s* and F 2*s* levels ($\sim$25 and $\sim$40 eV). For the materials with common H and F bonding sites, the H^+ and F^+ appearance potentials correspond to excitation of the C 2*s* level. The F^+ threshold is relatively weak, and a steep increase in the F^+ yield is observed near 40 eV (F 2*s* excitation). These results indicate that the final-state excitations leading to ion desorption in these systems are localized within functional groups but not necessarily within individual C–H or C–F bonds of the functional group.

I. INTRODUCTION

A number of recent studies of electron- and photon-stimulated desorption (ESD and PSD) of positive ions from organic molecular solids[1-5] have concluded that the nature of the predesorption final states involves several valence holes. Experiments on a series of hydrocarbon molecules[4] indicated that such multivalence hole states gave rise to both H^+ and $CH_3{}^+$ desorption, were localized within methyl or other functional groups of the molecule, and resulted from the decay of a C 2*s* hole. Subsequent work on nonafluoroisobutane [$(CF_3)_3CH$] and 1,2,3,5-tetrafluorobenzene ($C_6F_4H_2$) showed that the H^+ appearance potential (27 ± 1 and 29 ± 1 eV, respectively) involves the excitation of the C 2*s* level, while the F^+ (and CF^+) appearance potentials (38–40 eV) are connected with excitation from the F 2*s* level.[5] These molecules contain separate H and F bonding sites; i.e., no carbon atom is bonded to both a fluorine and a hydrogen atom. Therefore, separate appearance potentials for H^+ and F^+ confirm only that these multivalence hole excitations are localized within $-CF_3$, or other functional groups within the molecule, but indicate nothing regarding localization of excitation within specific chemical bonds.[5] In order to address this question, we have measured H^+ and F^+ desorption as a function of electron excitation energy from two molecular solids which contain sites with one carbon bonded to both a fluorine atom and one or more hydrogen atoms, 1-fluorobutane (C_4H_9F) and fluorocyclohexane ($C_6H_{11}F$). We report these results and compare them to the previously reported results on $(CF_3)_3CH$ and $C_6H_2F_4$.

II. EXPERIMENT

The details of the experimental apparatus used in this Brief Report are described in detail elsewhere.[6] Briefly, gases are condensed through a 0.040-in.-i.d. doser tube onto a liquid-nitrogen-cooled metal substrate under ultrahigh vacuum (base pressure of 5×10^{-10} Torr). Dosing times and pressures were controlled so that thin noncharging overlayers were deposited.[4] The electrons are focused onto the target from an indirectly heated cathode. The electron-beam energy reported here is just the applied voltage of the cathode relative to the target metallic substrate Fermi level, corrected for the cathode work function and temperature of the thermionic emitter. Ions were detected using a quadrupole mass spectrometer and ion intensities were recorded using pulse counting techniques. Spectra were recorded in a series of scans with primary beam energy varied between $\sim$10 and 90 eV. Data were collected and stored on a computer. Beam currents were on the order of 20 nA/mm^2. In order to minimize beam damage and sublimation effects, the data presented here were taken on freshly dosed metal substrates.

III. RESULTS

H^+ and F^+ yields from $(CF_3)_3CH$ and $C_6H_2F_4$ as a function of primary beam energy are presented in Figs. 1(a) and 1(b). The ion yields are normalized to equal intensities at $\sim$60 eV above threshold in order to compare the shapes of the ion yield curves. The H^+ thresholds are 27 ± 1 and

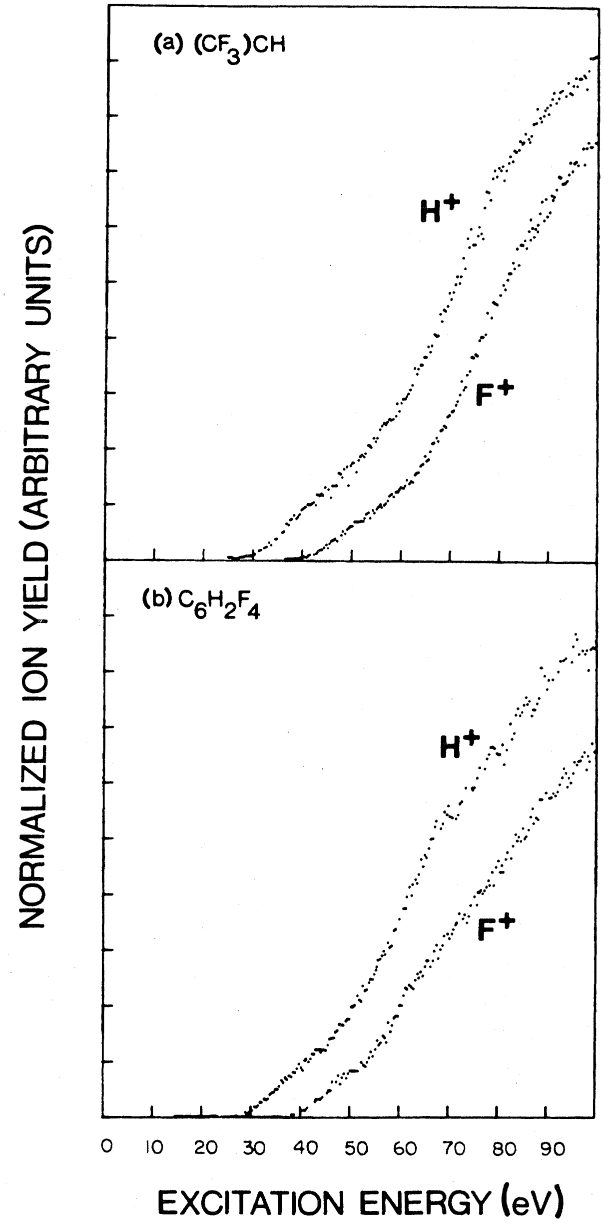

FIG. 1. H^+ and F^+ yields from (a) $(CF_3)_3CH$ and (b) $C_6H_2F_4$. Ion yield curves have been normalized to equal intensities at ~60 eV above threshold.

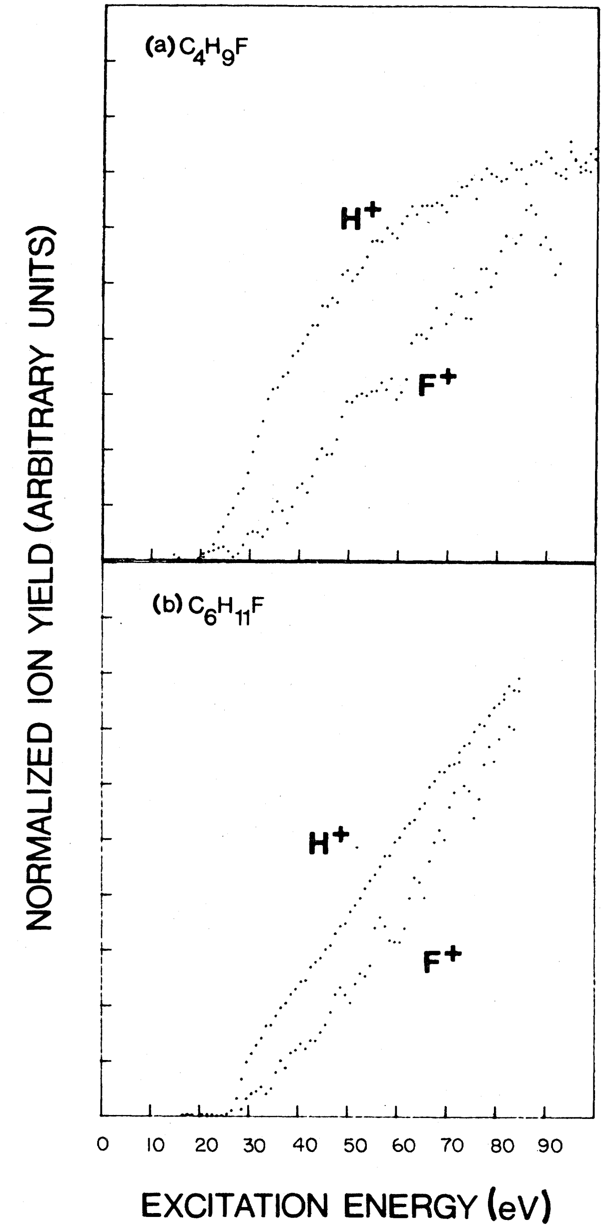

FIG. 2. H^+ and F^+ yields from (a) C_4H_9F and (b) $C_6H_{11}F$. Ion yield curves have been normalized to equal intensity at ~60 eV above threshold. F^+ data have been digitally smoothed.

29 ± 1 eV, respectively.[5] The F^+ thresholds are 40 ± 1 eV for $(CF_3)_3CH$ and 38 ± 1 eV for $C_6H_2F_4$.[5] Both H^+ yield curves exhibit a change in slope near 40 eV, the region of the F^+ threshold, but this feature is common to all hydrocarbon systems examined thus far[4,5] and should not be related to the F^+ onset. As previously discussed, the H^+ appearance potentials correspond to excitations from within the C 2*s* shell,[5] possibly to a Rydberg or antibonding level.[4,5,7] The F^+ appearance potentials are identified with excitations from the F 2*s* levels.[5,7–9] A notable feature of the data is, for each system, the similarity in shape of the H^+ and F^+ yield curves. For $(CF_3)_3CH$, both the H^+ and F^+ curves exhibit an inflection ~10 eV above the appearance threshold, a second inflection ~23 eV above threshold, and a third change in slope ~50 eV above threshold. For $C_6H_2F_4$, there is a change in slope ~20 eV above threshold for both H^+ and F^+ yield curves and a second change in slope ~40 eV above threshold.

The normalized H^+ and F^+ yields for C_4H_9F and $C_6H_{11}F$ are shown in Figs. 2(a) and 2(b). In contrast to $(CF_3)_3CH$ and C_6H_2F, there is a common appearance potential for H^+ and F^+ in both monofluorides. This threshold is 21 ± 1 eV for C_4H_9F and 24 ± 1 eV for $C_6H_{11}F$. For both materials the H^+ yield rises rapidly from this threshold with increasing beam energy while the F^+ yield increases relatively slowly until ~40 eV, at which time a more rapid increase in F^+ yield versus beam energy is observed. Above 40 eV, the shapes of the H^+ and F^+ curves are dissimilar for C_4H_9F.

For $C_6H_{11}F$, both H^+ and F^+ yields increase roughly linearly in the region above 40-eV energy. For C_4H_9F, the H^+/F^+ yield corrected for stoichiometry (at 70-eV beam energy) is ~8/1 while for $C_6H_{11}F$ the ratio is ~15/1.

IV. DISCUSSION

The (24 ± 1)-eV H^+ (and F^+) appearance potential for $C_6H_{11}F$ corresponds closely to the H^+ appearance potential observed for C_6H_{12} and corresponds to an excitation from within the C 2*s* shell.[10] The (21 ± 1)-eV threshold observed for C_4H_9F also corresponds to an exctitation from within the C 2*s* shell of that system.[11] The significance of the 3-eV shift in the H^+ (and F^+) appearance potential between C_4H_9F and $C_6H_{11}F$ is not understood, since the x-ray photoelectron spectroscopy (XPS)-determined binding energies of the C 2*s* "bands" in these compounds are very similar.[10,11]

The data presented in Figs. 1 and 2 indicate that when F and H atoms are attached to separate carbon centers, the H^+ desorption threshold coincides with excitation from the C 2*s* level and F^+ dissociates at an energy corresponding to F 2*s* excitation.[4,5] However, when a F atom and H atom are attached to the same carbon atom, a weak F^+ threshold is observed to coincide with the H^+ threshold (again coinciding with C 2*s* excitation) while a steep rise in F^+ yield is observed near the F 2*s* excitation threshold. An examination of the general electronic structure of fluorinated hydrocarbons indicates that an F^+ threshold at ~21–24 eV is surprising.

Photoemission[7,8] electron energy loss[7] and UV absorption measurements[7] and *ab initio* Hartree-Fock calculations for the gas-phase molecular series $CH_{4-x}F_x$ (Ref. 8) show that binding energies (relative to the vacuum level) of C-H bonding orbitals are ~12–13 eV; C–F bonding orbitals are at $\gtrsim 15$ eV; C $2s \rightarrow 3s, 3p$ excitations occur at ~21–24 eV; the C 2*s* ionization energy is 25 eV, and the F 2*s* orbitals are at ~40 eV. The same is generally true for fluorinated alkane polymers[9] except that the highest-lying C–H (and C–C) bonding orbitals are at ~9–10 eV (relative to the vacuum level). Previous ESD and PSD studies on organic thin films,[1,4,5] H on Ni,[12] and H on Si (Ref. 13) have concluded that final states leading to ion dissociation involve several valence holes. Assuming that final-state hole-hole repulsion is approximately canceled by the electron-hole interactions with a Rydberg electron, there is sufficient energy to allow decay from a C 2*s* hole to a final state with two holes in the C–H bonding orbitals, and this provides a rationale for the observed H^+ appearance potentials in the hydrocarbon and fluorinated hydrocarbons at energies corresponding to excitation of the C 2*s* level. Creation of the analogous final state with both holes in C–F bonding orbitals requires in excess of 30 eV of energy, so that F^+ appearance potentials (Fig. 1) or steep increases in yield (Fig. 2) at F 2*s* excitation energies are not surprising. The observed small F^+ desorption threshold at $\sim 21 \pm 1$ eV in C_4H_9F and 24 ± 1 eV in $C_6H_{11}F$ indicates that F^+ desorption can occur from a final state other than one involving two holes in C–F bonding orbitals. A possible explanation is that energy transferred to the system in creating the C 2*s* hole then is randomized throughout the system (or at least the functional group) in a manner analogous to the quasi-equilibrium theory (QET) statistical process observed for gas-phase hydrocarbons.[14,15] This is unlikely, however, as such a mechanism should result in both H^+ and F^+ desorption near the thrermodynamic minimum ~18 eV.[14] A more plausible explanation is that a C 2*s* hole can decay to a final state with one hole in a C–H bonding oribital and one in a C–F bonding orbital. The electronegativities of H, C, and F are such that a hole in a C–H and one in a C–F bonding orbital amount approximately to a hole on the carbon and a hole on the fluorine atom and could give rise to F^+ dissociation. This mechanism would then explain the failure to observe an ~(27–29)-eV F^+ threshold in $(CF_3)_3CH$ and $C_6H_2F_4$, where no F and H atoms are attached to the same carbon atom. In the absence of any information concerning, for example, ion kinetic energy distributions, nothing further can be said about the details of the dissociation mechanism. The fact that both C_4H_9F and $C_6H_{11}F$ exhibit sharp increases in F^+ yield at 40 eV indicates that in these systems, as in $(CF_3)_3CH$ and $C_6H_2F_4$, excitation of the F 2*s* level leads to F^+ dissociation. The structure present in both H^+ and F^+ dissociation for $(CF_3)_3CH$ and C_6H_2F at excitation energies $\gtrsim 50$ eV which are absent from C_4H_9F and $C_6H_{11}F$ suggest that more complex multihole excitations can also result in ion dissociation and that these excitations are sensitive to the system's chemical structure.

IV. SUMMARY AND CONCLUSIONS

ESD of H^+ and F^+ has been observed from condensed multilayers of $C_6H_2F_4$, $(CF_3)_3CH$, $C_6H_{11}F$, and C_4H_9F. Materials with separate H and F bonding sites [$C_6H_2F_4$ and $(CF_3)_3CH$] exhibit separate appearance potentials corresponding to C 2*s* and F 2*s* excitation energies, respectively. Materials with common H and F bonding sites ($C_6H_{11}F$ and C_4H_9F) exhibit a common H^+ and F^+ appearance potential corresponding to C 2*s* excitation. The F^+ threshold is relatively weak and a pronounced increase in the F^+ yield occurs near the F 2*s* excitation energy energy. This demonstrates that the multivalue hole excitations which induce ion desorption in these systems are localized within functional groups (e.g., CF_3, CH_2) of the molecule, but not necessarily within individual chemical bonds of the functional group.

ACKNOWLEDGMENT

This work was performed at Sandia National Laboratories, supported by the U.S. Department of Energy under Contract No. DE-AC04-DP00789.

---

[1] R. A. Rosenberg, V. Rehn, A. K. Green, P. R. LaRoe, and C. C. Parks, in *Proceedings of the First International Workshop on Desorption Induced by Electronic Transitions*, edited by N. H. Tolk, M. M. Traum, J. C. Tulley, and T. E. Madey (Springer, Berlin, 1983); see also R. Stockbauer, E. Bertel, and T. E. Madey, J. Chem. Phys. **76**, 5369 (1982).

[2] D. Hanson, R. Stockbauer, and T. E. Madey, J. Chem. Phys. **77**, 1569 (1982).

[3] R. Stockbauer, E. Bertel, and T. E. Madey, J. Vac. Sci. Technol. A **1**, 1162 (1983).

[4] J. A. Kelber and M. L. Knotek, Surf. Sci. **121**, L499 (1982).

[5] J. A. Kelber and M. L. Knotek, J. Vac. Sci. Technol. A **1**, 1149 (1983).

[6] M. L. Knotek and J. E. Houston, Surf. Sci. **91**, L17 (1980).

[7] M. B. Robin, *Higher Excited States of Polyatomic Molecules* (Academic, New York, 1974).

[8] C. R. Brundle and M. B. Robin, J. Chem. Phys. **53**, 2196 (1970).

[9] J. Delhalle, S. Delhalle, J. M. Andre, J. J. Pireaux, J. Riga, R. Caudano, and J. J. Verbist, J. Electron Spectrosc. Relat. Phenom. **12**, 293 (1977).

[10] B. E. Mills and D. A. Shirley, J. Am. Chem. Soc. **99**, 5885 (1977).

[11] J. J. Pireaux, R. Caudano, S. Svensson, E. Basilier, P.-A. Malmqvist, U. Gelius, and K. Siegbahn, J. Phys. (Paris) **38**, 1213 (1977).

[12] C. F. Melius, R. H. Stulen, and J. L. Noell, Phys. Rev. Lett. **48**, 1429 (1983).

[13] H. H. Madden, D. R. Jennison, M. M. Traum, G. Margaritondo, and N. G. Stoffel, Phys. Rev. B **26**, 896 (1982).

[14] H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, Proc. Natl. Acad. Sci. U.S.A. **38**, 667 (1952).

[15] C. Lifshitz, Adv. Mass Spectrom. **7**, 3 (1977).