Assignment of Electronic Transitions in the Fluoromethanes. A Bond Exciton Interpretation[1]

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Abstract: The vacuum ultraviolet spectra of the fluoromethanes are presented. The absolute intensities are obtained; the lower energy bands are found to increase nearly linearly in total intensity as each C–F bond is replaced by a C–H bond. The bond exciton model is used to interpret the results. The onset of absorption is shown to correlate with the ionization potential of each compound.

Electronic transitions involving molecular electrons pictured as localized in σ bonds are readily predicted by simple valence theories. However, detailed calculations suitable as aids in assigning observed transitions are still not reliable at this time owing to the very large number of electrons which have to be considered in even the simplest all-σ-bond molecules. In an attempt to assign molecular transitions of all types, the practice of comparing low-resolution spectra of a series of related compounds, and looking for trends or consistent patterns, has met with some success. In this spirit, we consider here an especially interesting series, the vacuum ultraviolet spectra of the fluoromethanes.[3–5] Paying particular attention to intensities, we find that this series strongly suggests use of a bond exciton model as an aid in assigning the transitions. This model, where it is applicable (*i.e.*, when electrons in bonds can be considered as practically localized; see below), is especially useful for the assigning of transitions, since one may proceed in a fashion dictated entirely by the spectra themselves, without requiring knowledge of the detailed mathematical form of the wave functions.[6,7] At the risk of duplication, all of the spectra discussed are shown to aid in the presentation.

Experimental Section

All the spectra contained herein were repeated on the same instrument (described elsewhere);[6] it is therefore felt that the relative intensities are quite reliable. The spectra were recorded on Kodak 103-0 photographic plates; the plates were in turn read upon a Joyce-Loebl Model MK IIIB recording microdensitometer.[8] Resolution of approximately 2 Å is achieved in general; however, lines in the Lyman source in the energy range above 80,000 cm^{-1} may render measurement of band positions and contours less certain than is implied by the resolution. Intensity measurements are also affected, but still the absolute intensities should be good to 25%. The sources and handling of chemicals used are listed in Table I.

Table I. Sources of Chemicals[a]

Compound	Source
CH_4	Phillips Research Grade (99.52%)
CH_3F	Peninsular ChemResearch
CH_2F_2	Peninsular ChemResearch
CHF_3	Matheson
CF_4	Matheson

[a] All chemicals used were vacuum distilled.

Results and Discussion

Cook and Ching[9] and Zobel and Duncan[4] have taken the spectrum of CF_4, and both results indicate absorption beginning at about 950 Å with a maximum at 900 Å (111,000 cm^{-1} = 111 kK). In agreement with this, no absorption was observed down to the LiF cutoff at 95 kK. Thus the first absorption in CHF_3 at around 87 kK must be associated with the C–H unit, since the nearest absorption band related to the CF_3 group must come at much higher energy; the transition may be thought of as essentially localized in the C–H bond. The theoretical interpretation of the spectra employed in this paper relies on this hypothesis; indeed, the fluoromethane series appears to be an ideal testing ground for the independent systems (or bond exciton) model.[10]

In order to illustrate the independent systems approach, we consider CH_2; see Figure 1. Isolated regions, roughly corresponding to the classical concept of a bond, are governed by local Hamiltonians; electrons in these regions interact (through at least electrostatic dipole–dipole terms) by an amount β. The secular equation is simply

$$\begin{vmatrix} \alpha - \lambda & \beta \\ \beta & \alpha - \lambda \end{vmatrix} = 0$$

where α is the localized, unperturbed excitation energy, for example, the transition energy at 87 kK in CHF_3, presumably due to the $(\sigma \rightarrow \sigma^*)_{C-H}$ transition. In this simple treatment, the effect of the fluorines, with markedly different α's, will be neglected but considered later. For CH_2 one obtains the splitting pattern depicted in Figure 2, while the intensity distribution is a function of the geometry. Assuming tetrahedral angles and longitudinal polarization of the local transition, the B_2 component is expected to possess two-thirds of the total intensity, the A_1 component one-third. Proceeding in a similar manner for the rest of the series, one obtains the results summarized in Figure 3. It should be mentioned that the oscillator strengths, acquired prior to any

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[2] Texaco Fellow, 1967–1968.

[3] P. Wagner and A. B. F. Duncan, *J. Am. Chem. Soc.*, 77, 2609 (1955).

[4] C. R. Zobel and A. B. F. Duncan, *ibid.*, 77, 2611 (1955).

[5] S. Stokes and A. B. F. Duncan, *ibid.*, **80**, 6177 (1958).

[6] J. W. Raymonda and W. T. Simpson, *J. Chem. Phys.*, 47, 430 (1967).

[7] R. H. Partridge, *ibid.*, 49, 3656 (1968).

[8] We thank Professor Aaron Novick for the loan of this instrument.

[9] G. R. Cook and B. K. Ching, *J. Chem. Phys.*, 43, 1794 (1965).

[10] The bond exciton model has been developed in ref 6 and 7. Only those features immediately applicable to the discussion will be outlined here.

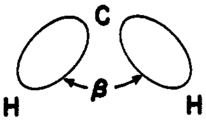

Figure 1. β represents the electronic interaction between "independent" bonding regions.

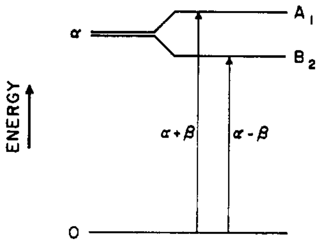

Figure 2. Energy level diagram for CH_2. The electronic states of the system are represented by their symmetry under C_{2v}.

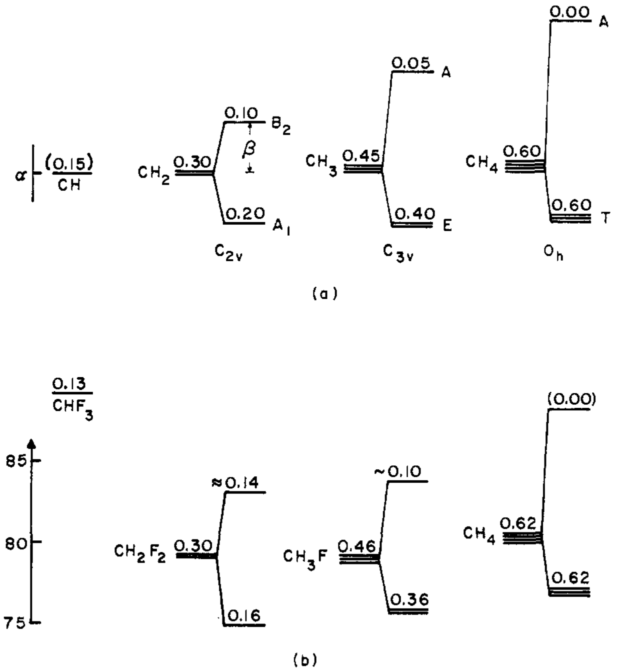

Figure 3. (a) Idealized CH_n system. (b) Observed $CF_{4-n}H_n$ system. Total oscillator strengths appear above the zero interaction levels; individual oscillator strengths appear above lines representing peak maxima. Experimental oscillator strengths are accurate to about 10% except where indicated more approximate; in these cases reliable intensities could not be obtained due to uncertainties in underlying background. Values in parentheses are defined.

calculations, were obtained by subtracting out the background tails of higher energy transitions and assuming symmetrical band contours. The possible contribution of small, forbidden transitions at the low-energy edge of the first absorption has been neglected.[11]

Referring to Figure 3b, one observes the nearly linear increase in total intensity as each new C–H unit is added, as well as the moderately successful predictions of the relative intensities. It should be noted that the vibrational structure appears only on the A-symmetry bands; the fact that methane shows no vibrationally structured bands supports the prediction that the A-component band is forbidden. Note also that in order for the intensity of methane to be in harmony with the rest of the series, one must assume that the bands with T symmetry are all included in a peak centered symmetrically at 78 kK. Heretofore, this had not been clear.

A preliminary study of the vibrational structure in these compounds seems to confirm the work done earlier by Duncan, *et al.*[3–5] However, the regularity of the vibrational spacing and peak intensities in CHF_3 suggests a possible alternative assignment based only on ν_3, the symmetrical deformation mode, with an excited state value of 400 cm^{-1}.

Let us consider the first transition in CHF_3 in more detail. It is almost surely due to the C–H unit and above is assigned as the $(\sigma \rightarrow \sigma^*)_{C-H}$ with longitudinal polarization.[12] However, one should not overlook the fact that this first transition in CHF_3 is comparable in energy with the first transition in atomic hydrogen; such a correspondence suggests a Rydberg-type transition localized on the hydrogen atom. In hydrogen, the first transition comes at $^3/_4$IP. If the CHF_3 molecular ionization potential differs from that of the hydrogen atom by only a small amount, and if the first ionization potential and the first transition are due to hydrogen, then $^3/_4$IP should be a good approximation to the initial absorption. That is

$$\text{H atom } (n = 2 \longleftarrow n = 1)\text{IP}^{13} = {}^3/_4(13.60 \text{ eV})^{14} = 82.3 \text{ kK}$$

$$CHF_3\ (n = 2 \longleftarrow n = 1)\text{IP} = {}^3/_4(13.84 \text{ eV})^{5} = 83.7 \text{ kK}$$

For the latter, the 0–0 band is observed at 82.8 kK. One might also consider the 3s ← 2p transition energy on the carbon atom. In atomic carbon, it falls at 59.7 kK,[15] but the molecular involvement appears to shift this far to the blue; for example, there is no absorption in CF_4 until 105 kK. Hence Rydberg-like transitions significantly involving the carbon atom appear unlikely. The σ^*_{C-H} would appear to have a large contribution from the $n = 2$ orbital on the hydrogen. To test such a hypothesis, consider CH_2F_2.

$${}^3/_4\text{IP} = {}^3/_4(12.55 \text{ eV})^5 = 75.9 \text{ kK}$$

The two transitions (one localized in each C–H bond) are expected to interact, and using a $\beta \simeq 4$ kK found from the splitting of the maxima, one predicts the first absorption to come at 71.9 kK. The absorption actually begins at about 70.9 kK; see Figure 4. Using CH_2F_2 as a prototype for the rest of the series and recognizing that in all cases (except CHF_3) the first transition is one β lower than the isolated bond transition energy because of the bond exciton splitting (see Figure 3a), a

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(11) Raymonda and Simpson predicted the forbidden charge-transfer transitions to be in this region; in fact, their spectra show evidence that they do occur.[6] Such transitions are expected to increase in intensity as the number of C–H bonds increases. This accounts, at least in part, for the somewhat larger than expected intensity in the "first" transition of CH_3F and CH_4.

(12) Longitudinal polarization for $\sigma \rightarrow \sigma^*$ transitions is predicted by all simple theories of valence.

(13) Adiabatic ionization potentials will be used throughout this paper.

(14) "Tables of Ionization Potentials," U. S. Atomic Energy Commission, June 20, 1960.

(15) H. E. White, "Introduction to Atomic Spectra," McGraw-Hill Book Co., Inc., New York, N. Y., 1934.

comparison of $^3/_4$IP is made with the 0–0 band in Table II.[16] Note how well the 0–0 bands follow the ionization potentials. Since several of the ionization potentials were determined from very short Rydberg series, caution should be exercised in interpreting these results; nevertheless, it would appear that the energy of what is called the $(\sigma \rightarrow \sigma^*)_{C-H}$ transition is closely associated with the promotion energy $n = 2 \leftarrow n = 1$ of the hydrogen atom.

Table II. An Illustration of How the First Absorption Maximum (max) Parallels the Ionization Potential[a]

Compound	IP,[5] eV	$^3/_4$IP, kK	$^3/_4$IP β-corrected	0–0 band (max − Δ)
CHF_3	13.84	83.7	83.7	82.8
CH_2F_2	12.55	75.9	71.9	70.9
CH_3F	12.80	77.4	73.4	71.5
CH_4	12.95	78.3	73.4	73.5

[a] The average value of β was found to be about 4kK, while the best value for Δ was taken to be 4.5kK.

The basic theory, which is sufficient to explain the gross aspects of low-resolution, σ-bond spectra, has, in fact, oversimplified the problem. Raymonda and Simpson[6] and Partridge[7] in their working model assumed only dipole–dipole terms contributing to β; they further assumed these classical dipoles to be located in the center of the bonds leading to large (~28 kK) bond exciton interactions. However, as observed above, the σ^*_{C-H} has a sizable contribution from the hydrogenic Rydberg orbital, and the transition dipole may be centered near the hydrogen nucleus. This would reduce the interaction to a value in line with that found here. Furthermore, exchange cannot be ignored, for the overlap integrals between two hydrogen atoms in ethane is not negligible (0.269),[17] particularly in the excited state.[18] In addition, one must consider the C–F units, especially the permanent dipoles of these bonds, for they surely interact with the transition dipoles of the C–H bonds. The inclusion of a permanent dipole into the transition dipole–dipole interaction scheme is complicated by a phase ambiguity. Also, the usual blue shift of the spectral features accompanying a fluorine substitution seems to be violated in going from CH_4 to CH_3F to CH_2F_2. Hence, one β for all compounds cannot be found—not an unexpected result—and attempts to calculate β have given only an order-of-magnitude result.

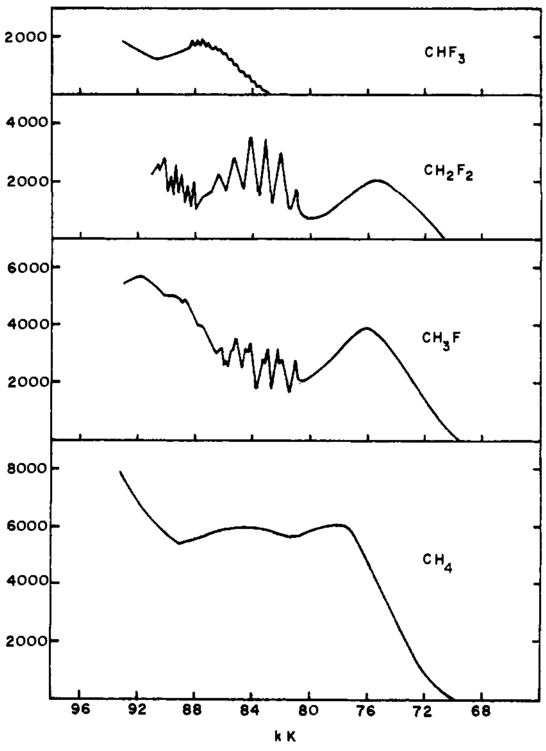

Figure 4. The observed fluoromethane spectra. Abscissa in kK (1 kK = 1000 cm^{-1}); ordinate is absolute intensity measured in l. (mole cm)$^{-1}$.

Conclusions

The series of methyl fluoride spectra strongly suggests application of the bond exciton model. That is, the linear increase in intensity of the above assigned $(\sigma \rightarrow \sigma^*)_{C-H}$ transitions as each new hydrogen replaces a fluorine atom supports the intuitive concept of a localized bond; the apparent splitting and intensity patterns demand a longitudinal polarization assignment while the close correspondence of the first absorption with the ionization potential indicates that these transitions have a strong hydrogenic-Rydberg dependence.

The practice of fluorine substitution in small molecules to expose lower energy transitions may prove to be a useful technique of wide application.

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(16) Since we are using adiabatic ionization potentials, one might plausibly refer to the 0–0 bands. But as the number of C–H bonds increases, weak charge-transfer bands, predicted to come slightly to the red of the first allowed transition,[6,7] probably become important. Thus the onset of absorption may not correspond to the 0–0 band, especially in CH_3F and CH_4. Where the 0–0 band appears to be well defined, CHF_3 (82.8 kK) and probably CH_2F_2 (70.9 kK), it comes about 4.5 kK below the band maximum. Thus a Δ of 4.5 kK will be subtracted from the easily identifiable band maxima in order to approximate the location of the 0–0 bands (see Table II).

(17) J. A. Pople and D. P. Santry, *Mol. Phys.*, **9**, 301 (1965).

(18) D. Peters, *J. Chem. Phys.*, 41, 1046 (1964).