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The Vacuum Ultraviolet Absorption Spectrum of Difluoromethane[1]

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The absorption spectrum of CH_2F_2 was investigated in the region 535 to 2200 Å. with a reciprocal dispersion of about 4.14 Å. per mm., and high resolving power. Four resolved electronic transitions were found with origins at approximately 1335, 1237, 1135 and 987 Å. Below 934 Å. and extending to at least 535 Å., a region of continuous absorption was observed. The transitions at 1335 and at 987 Å. showed no resolved vibrational structure, while the transitions at 1237 and at 1135 Å. showed well resolved vibrational structure. A tentative analysis of the vibrational patterns is presented, and the nature of the electronic transitions is discussed.

Electronic transitions in the halogen derivatives of methane lie principally in the vacuum ultraviolet region, and have not been completely investigated. The spectrum of CH_2F_2 in this region has not been reported previously. In the present paper a detailed description of the spectrum of this molecule is presented. Results of similar investigations of CF_4, CCl_2F_2, CH_2Cl_2, CCl_4 and $CHCl_3$ will be reported in a subsequent paper.

Experimental Details

Most of the spectra were obtained from a two-meter radius of curvature grating, ruled 30000 lines per inch. The grating was mounted at about normal incidence in a vacuum and gave a reciprocal dispersion of about 4.14 Å./mm. in the first order. The Lyman discharge was used as source of continuous background. It was operated by the discharge, once a second, of a one microfarad capacitor charged to 15,000 volts. Helium was used as the carrier gas. The vapor was contained in the spectrograph, which afforded a path length of about four meters. The pressure of the vapor was varied systematically by small increments from 0.001 to 0.5 mm. At higher pressures, the smaller volume of a vacuum spectrograph with a one meter radius, 30000-line-per-inch grating was more convenient. A maximum pressure of 140 mm. vapor was used with the smaller spectrograph, with a path length of about two meters. A conventional H_2 discharge, separated from the vapor in the spectrograph by a LiF window, was used in the high pressure investigations. The only additional information obtained at high pressures concerned long wave length limits.

The spectra were photographed on Eastman Kodak Company SWR plates or films. The plates were measured on a comparator in the usual way against internal standard emission lines[3] present in the discharges.

The CH_2F_2 was obtained from the Kinetic Chemicals Company, who furnished the following information about the purity: "the sample was carefully fractionated and has a boiling point of −51.7°. Analysis by means of an Infrared Spectrophotometer indicates that the sample contains 0.02 to 0.03 mole % of CHF_3 and 0.05 mole % of $CHClF_2$." The method used to obtain low pressures in the spectrograph would be expected to further fractionate the sample, but no change with time was observed in the vacuum ultraviolet absorption spectrum. While there is always the possibility that some impurities are left, it is believed that all of the observed spectra belong to CH_2F_2.

Experimental Results

The spectrum was investigated throughout the pressure range 0.001 to 0.500 mm. in the two-meter spectrograph (535–2225 Å.), and from 0.010 to 140 mm. in the one-meter spectrograph (1650–2400 Å.). Four separate electronic transitions were found. The longest wave length transition, with a maximum at 74855 cm.$^{-1}$, is a region of continuous absorption. The next two transitions at 80856 and 88144 cm.$^{-1}$ are accompanied by considerable vibrational structure. The fourth transition, with a maximum at 101286 cm.$^{-1}$ is continuous. A continuous absorption begins at approximately 107000 cm.$^{-1}$, beyond which nothing can be resolved. This limit is observed first at about 0.003 mm. It is believed that this limit, which is not sharp, is not an ionization limit, but the beginning of another electronic transition overlapped by many other transitions converging to the lowest and higher ionization potentials of the molecule.

The pressure dependence of the spectrum is roughly as follows. The transition at 101286 cm.$^{-1}$ is seen clearly first at 0.004 mm. and the structure of the 80856 and 88144 cm.$^{-1}$ transitions begins to appear at about the same pressure. At 0.006 mm. the 101286 cm.$^{-1}$ transition merges with the continuous absorption at higher frequencies. The transitions with structure are fully developed at 0.010 mm., and the 74885 cm.$^{-1}$ transition first appears. As the pressure is increased, all these transitions merge, until at 0.060 mm. only a low frequency limit at 74885 cm.$^{-1}$ is present. This limit is gradually shifted to lower frequencies with increase of pressure, until at 140 mm. it is at 56625 cm.$^{-1}$ in a two meter column.

The structure of the 80856 and 88144 cm.$^{-1}$ transitions is shown in Figs. 1 and 2, which are adapted from microphotometer tracings. The maxima of the vibrational transitions, or the central minima of double headed vibrational transitions are given in Table I, with a tentative assignment. In this assignment the notation of Rank, Shull and Pace[4] is adopted.

TABLE I

A. STRUCTURE OF THE 80856 CM.$^{-1}$ TRANSITION

Frequency (cm.$^{-1}$)	Assignment
80856	ν_0
82008	$\nu_0 + \nu_3$
83109	$\nu_0 + 2\nu_3$
84209	$\nu_0 + 3\nu_3$
85250	$\nu_0 + 4\nu_3$
86224	$\nu_0 + 5\nu_3$

B. STRUCTURE OF THE 88144 CM.$^{-1}$ TRANSITION

Frequency (cm.)	Assignment
88144	ν_0
88512	$\nu_0 + \nu_4$
88959	$\nu_0 + 2\nu_4$
89301	$\nu_0 + \nu_3$
89726	$\nu_0 + \nu_3 + \nu_4$
90137	$\nu_0 + \nu_3 + 2\nu_4$
90515	$\nu_0 + 2\nu_3$
90963	$\nu_0 + 2\nu_3 + \nu_4$
91309	$\nu_0 + 2\nu_3 + 2\nu_4$

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(2) Part of a dissertation presented to the Faculty of the Graduate School of the University of Rochester in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) "Provisional Wavelength Identification Tables for the Vacuum Ultraviolet," J. C. Boyce and J. T. Moore, Massachusetts Institute of Technology, Cambridge, Massachusetts. Mimeographed for private distribution, 1941.

(4) D. H. Rank, E. R. Shull and E. L. Pace, *J. Chem. Phys.*, **18**, 885 (1950).

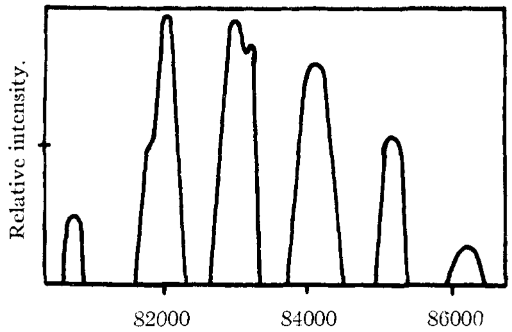

Fig. 1.—The 80856 cm.$^{-1}$ transition in CH_2F_2.

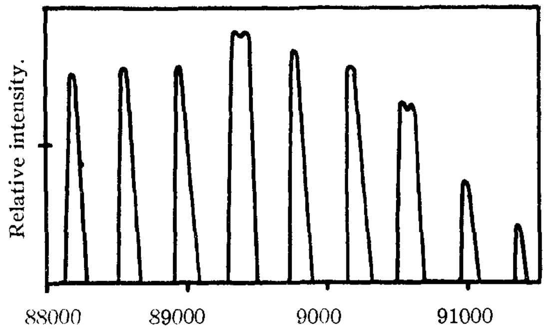

Fig. 2.—The 88144 cm.$^{-1}$ transition in CH_2F_2.

Discussion

The 80856 cm.$^{-1}$ transition consists of six relatively wide-spaced members. The frequencies can be fitted within experimental error of measurement to the approximate formula

$$\nu = 80856 + 1173v - 19.7v^2$$

The bands with v = 1,2 show double intensity maxima and indications of this appear also in v = 3 and possibly other members. The double maxima appear to be associated with unresolved rotational structure, and the presence of central minima suggests that the transition moment is perpendicular to the principal axis of inertia.[5] Consequently the frequency of approximately 1173 cm.$^{-1}$ should be identified with a type a_1 or b_2 vibration. Since several quanta of the same vibration are excited, the type a_1 is more probable. There are two normal state vibrations of this type[4,6] which might be modified to about 1173 in the excited state. These are ν_2 = 1508 cm.$^{-1}$, associated with bending modes of F–C–F and H–C–F groups and ν_3 = 1078 cm.$^{-1}$, associated with C–F stretching. There does not appear to be any really satisfactory basis for choice. However in CH_2Cl_2 there is an analogous transition where a progression in ν_3 appears prominently. Accordingly the 1173 cm.$^{-1}$ frequency is tabulated as ν_3.

The 88144 cm.$^{-1}$ transition consists of nine vibrational members. The average separation is uniform, about 400 cm.$^{-1}$, and these vibrational transitions could be assigned most simply to harmonics of ν_4-(a_1), an F–C–F deformation frequency, which has a normal state value of 529 cm.$^{-1}$. However the fourth and seventh members of the progression show the doubled-headed structure of members of the 80856 cm.$^{-1}$ transition. Furthermore the separation between v = 0 and v = 4 is 1157, while the separation between v = 4 and v = 7 is 1214 cm.$^{-1}$. For this reason the assignment in Table I is preferred. The actual mode may be ν_2 instead of ν_3, as in the 80856 cm.$^{-1}$ transition.

The two transitions at 74855 and 101286 cm.$^{-1}$ appear to be perfectly continuous under the same conditions of pressure, path length and resolving power used to show structure in the other transitions. While it is possible that the upper states involved are unstable toward decomposition, it is believed that the continuous nature is only apparent, and is due to excitation of many overlapping vibrations. In general no satisfactory decision can be made on this point for polyatomic molecules, since the resolving power needed for a decision is probably unattainable. Nevertheless it is of interest to see what conclusions, if any, can be drawn about the difference in character of electronic excitation in the continuous transitions and in the (discrete) transitions accompanied by vibrational structure.

Symmetry arguments cannot be used in this case, because the symmetry is not very high and no possibility of degenerate states exists. Instead, qualitative arguments based essentially on extension of the Franck–Condon principle to polyatomic molecules should be used. It is assumed that the electron excited in the discrete transitions has a high probability of being found in a particular part of the lower potential surface. In a LCAO molecular orbital description the electron might come from an orbital made mostly from contributions of the atomic orbitals attached to a few atoms, and be largely localized, for example, in the C–F bond region. A similar region of the upper potential surface may be reached by absorption. The latter region is displaced relative to the lower region to account for the long progressions, but is separated from other regions by barriers of suitable height. In other words, the process of electronic excitation may resemble closely excitation in a diatomic molecule. This concept of localized transitions is not new, but it has not usually been applied to such small molecules.[7] From the same viewpoint, the continuous transitions are non-localized transitions. The electron is not localized in any particular part of the molecule with a high probability, and transitions may occur to a larger number of possible parts of the upper surface. As a result, a larger number of vibrations may be excited to produce the appearance of continuous absorption, and the probability of reaching directly or indirectly a dissociation region of the upper surface is greater.

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(5) H. B. Stewart and H. H. Nielsen, *Phys. Rev.*, **75**, 640 (1949).

(6) E. L. Pace, *J. Chem. Phys.*, **18**, 881 (1950).

(7) The idea of localized molecular orbital functions is not, of course, new: see "Valence," C. A. Coulson, Oxford University Press, 1952, Chap. VII.