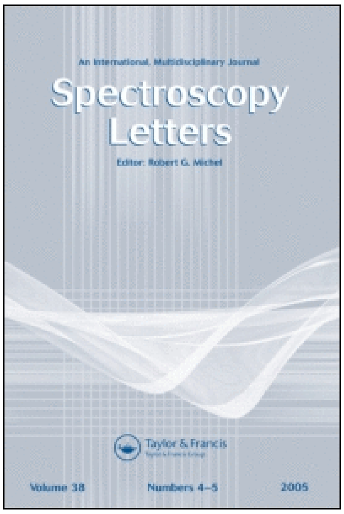

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Vacuum Ultraviolet Absorption Spectrum of Difluoromethane Reinvestigated

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ABSTRACT The vacuum ultraviolet (VUV) absorption spectrum of difluoromethane (CH_2F_2) was studied using synchrotron radiation from the storage ring Indus-1, Indore, India. Spectra were recorded in the spectral region 1050–1500 Å (~8.3–11.8 eV) at a resolution of 1.5 Å. Three absorption band systems were observed in this region. Overall features observed are in good agreement with previously published work. Some discrepancies in assignments of the observed vibronic bands carried out by previous workers have been resolved. The observed bands have been classified in terms of Rydberg series.

KEYWORDS difluoromethane, photoabsorption, synchrotron, vacuum ultraviolet

INTRODUCTION

Difluoromethane belongs to the family of molecules known as hydrofluorocarbons, or HFCs, which are widely used in the refrigeration industry. HFCs do not contain chlorine, which is responsible for the catalytic destruction of ozone in the stratosphere, therefore they are considered to have an ozone depletion potential of zero. Moreover, HFCs are subjected to removal in the troposphere by reaction with hydroxyl radicals, thus considerably reducing their lifetime in the troposphere compared with that of the more stable CFCs.[1] Under the Montreal protocol, use of CFCs has already been phased out. The intermediate replacement compounds, HCFCs (hydrochlorofluorocarbons), which although less dangerous to the ozone layer, still contain chlorine and hence are not acceptable substitutes in the long run. HCFCs are to be completely replaced by HFCs by the year 2030. Although HFCs do not pose a threat to the ozone layer, their release into the atmosphere is of concern as they are greenhouse gases, with strong IR absorption. Because large quantities of these molecules are likely to be released into the atmosphere over the next few decades, it is also important to study their interaction with radiation in other regions of the electromagnetic spectrum (e.g., the far UV). It is also known that many reactions in the atmosphere proceed via formation of highly excited states, typically lying in

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the VUV and soft X-ray regions. Spectroscopic studies of these high-lying electronic states form important inputs in understanding the chemistry of CH_2F_2 in the atmosphere. Synchrotron radiation being intense and tunable across the entire VUV region is an ideal source for such studies. It has been pointed out that the synchrotron radiation continuum mimics the solar emission continuum, thus making it especially suitable for studying problems of atmospheric interest.[2]

The VUV absorption spectrum of CH_2F_2 was first reported by Wagner and Duncan using a Lyman discharge continuum source in 1955.[3] Subsequently, there have been several reports of VUV absorption spectra of fluoromethanes using conventional laboratory sources.[4–6] The only photoabsorption study to date using synchrotron radiation is by Seccombe et al.[7] Photoelectron studies have been carried out by Brundle et al.[8] and Pradeep and Shirley.[9] A variety of theoretical calculations have been performed on the electronic states of CH_2F_2.[10–13] Recently, valence shell orbital momentum profiles have been investigated by binary (e, 2e) spectroscopy by Su et al.[14] A closer study of these reports, however, shows several discrepancies and incompleteness in assignment of the vibronic transitions observed. For instance, even the ordering of the valence orbitals reported in various papers differs. The spectral analysis reported in some of the papers was found to have several inconsistencies and errors. A re-investigation of the VUV absorption spectrum of CH_2F_2 using synchrotron radiation was taken up to resolve these issues.

MATERIALS AND METHODS

Experiments were carried out on the Photophysics Beamline at the 450-MeV storage ring Indus-1 at RRCAT (Indore, India). A 1 meter Seya–Namioka monochromator is used in this beamline for wavelength scanning. With a 2400 g/mm ion etched laminar grating mounted in the monochromator, the resolution achieved is estimated to be about 1.5 Å. The ruled area of the grating is 50 × 30 mm, and the reciprocal linear dispersion is about 4 Å/mm. mm. Details about the beamline have been discussed elsewhere.[15,16] The gas phase absorption cell used in the current study is basically a 6-way stainless steel cross pumped to a vacuum of the order 10^{-6} mbar by a turbomolecular pump and connected to the beamline via a gate valve with a LiF window fitted in it. This enables us to carry out gas phase experiments in the wavelength region of 1050–2000 Å without disturbing the vacuum in the beamline. Radiation passing through the cell is incident on a sodium salicylate-coated quartz window used as a wavelength shifter converting VUV light to visible light, which in turn is detected by a photomultiplier (model 9425 QB, Electron Tubes, UK). Pressure is measured using a capacitance gauge (Pfeiffer model CMR262). At every step of size 0.5 Å, the storage ring beam current is recorded to normalize the intensity with respect to the decaying beam current. Wavelength scanning and data collection is done by means of a computer-controlled data acquisition system.

The CH_2F_2 sample (stated purity 99.9 9%, Matheson) was contained in a glass flask connected to the cell through suitable glass–metal adapters. Sample pressure inside the cell is controlled with the help of standard SS Swagelok (USA) valves. Prior to every set of experiments, the stainless steel cell is cleaned ultrasonically, leak-tested, and then reassembled onto the beamline. During the process of evacuating it using a turbomolecular pump, it is also baked for a few hours at a temperature of about 150°C. In order to ascertain that all contaminants are thoroughly removed and there is no leak from the outside, a blank spectrum of the empty cell is recorded in the entire VUV region from 1050 to 2000 Å before starting the experiment to find out the presence/absence of residual gases like CO_2 or water vapor, which have a strong VUV absorption. Residual impurities in the sample are removed by subjecting it to a freeze-pump-thaw cycle before introduction into the cell. Reference transmission spectra were recorded through the empty cell (I_0). The transmission spectrum with sample gas filled in the cell serves as I. Using the Beer–Lambert law, $I = I_0 e^{-\mu x}$, a plot of $\ln(I_0/I)$ versus wavelength generates the absorption spectrum.

The VUV absorption spectrum of CH_2F_2 was recorded in the wavelength region 1050–1500 Å at several pressures. VUV photoabsorption lines of Kr and Xe were used for wavelength calibration. The VUV absorption spectrum of Xe is shown in Figure 1. By fitting the experimentally observed lines to different line profiles, the average spectral resolution was found to be ~1.5 Å.

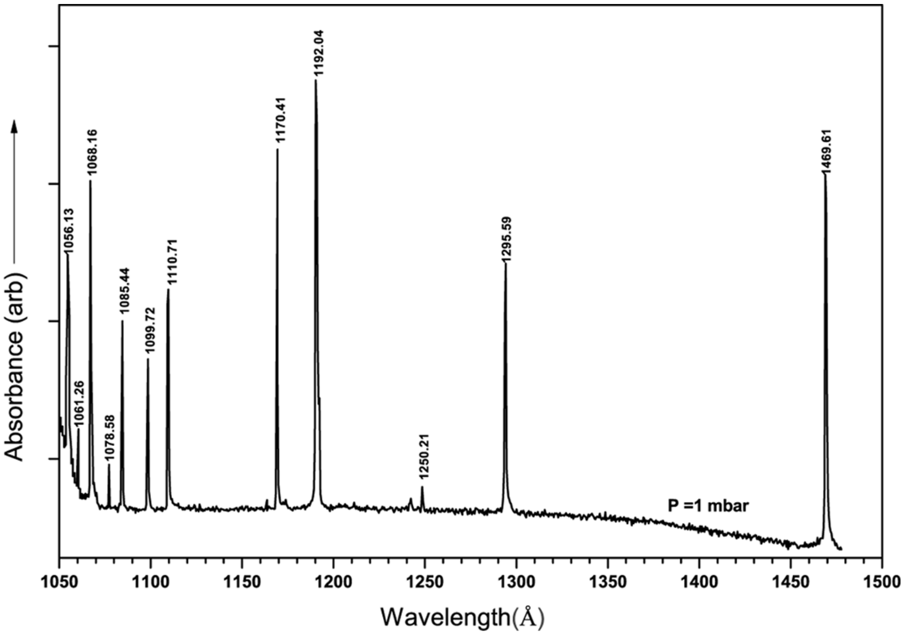


FIGURE 1 The VUV Absorption spectrum of Xenon in the spectral region 1050–1500 Å recorded at Photophysics Beamline, Indus-1.

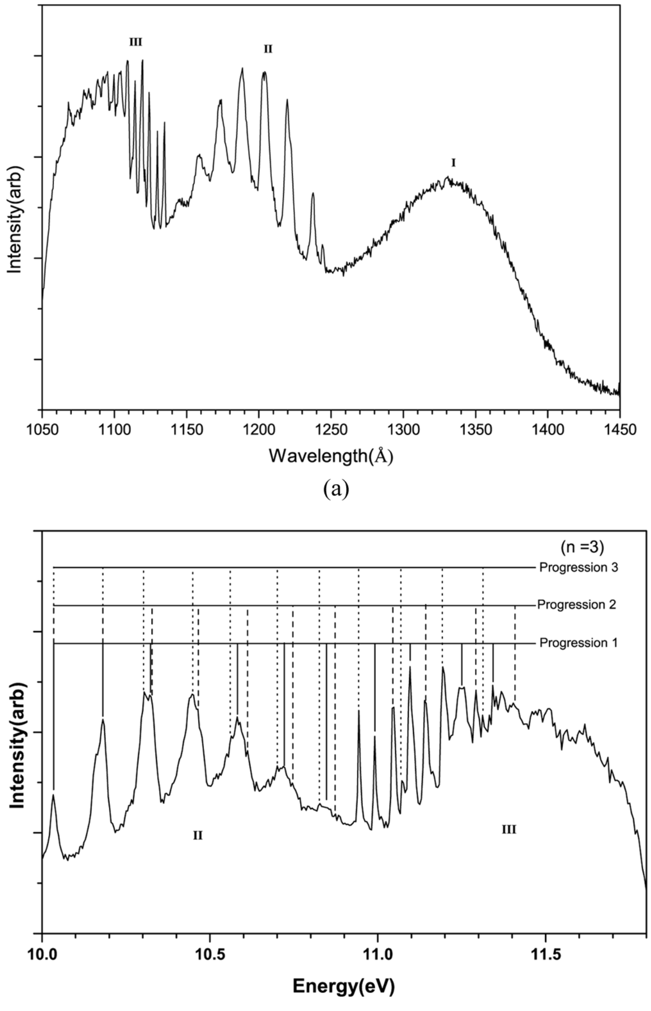
RESULTS AND DISCUSSIONS

CH_2F_2 belongs to the C_{2v} point group and its ground state ($^1A_1$) electronic configuration is $(1a_1)^2 (1b_1)^2(2a_1)^2(3a_1)^2(2b_1)^2(4a_1)^2(1b_2)^2(5a_1)^2(3b_1)^2(1a_2)^2 (4b_1)^2(6a_1)^2(2b_2)^2$.[8,10,11] Here it is relevant to point out that the ordering of the outermost orbitals has been reported differently by different authors. We have adopted the orbital ordering given by Brundle et al.[8] and followed by several other authors. The most loosely bound orbital viz. the $2b_2$ orbital has a strong CF antibonding and CH bonding character. Based on earlier studies,[8] the first three electronic transitions are expected to be $2b_2$–3s, $2b_2$–3p, and $6a_1$–3s, where the Rydberg orbitals 3s and 3p are expected to show characteristics of fluorine atomic orbitals.

The VUV absorption spectrum of CH_2F_2 in the region 1050–1500 Å (8.3 to 11.8 eV) recorded at the Indus-1 storage ring facility is shown in Figure 2a. Three electronic transitions can be clearly seen in this region in excellent agreement with previous studies. These are marked as I, II, and III in the figure, starting from the lower energy end moving to the higher energy end of the spectrum. Absorption bands can be properly distinguished down to approximately 1070 Å (11.6 eV), below which the data become unreliable due to the transmission edge of the LiF window. A pressure of 0.01 mbar is found to be optimum giving rise to clearly discernible absorption features. All the three absorption features have been assigned in terms of Rydberg series. Figure 2b shows an expanded view of the band systems II and III in energy scale (eV) with the three progressions marked.

The first absorption feature (I) is a continuum starting at about 1450 Å (8.6 eV) with peak at about 1330 Å (9.3 eV). This has been assigned to the transition $2b_2$–3s. The lack of any vibrational structure in this band indicates that the change in geometry of the molecule in the excited state if any is very minimal. This band has been assigned previously to a Rydberg series.[7] We agree with this assignment and have calculated the positions of the higher members of this Rydberg series, which is shown in Table 1. In the second system (II), a total of seven bands can be clearly distinguished, as against six bands reported previously. This set of bands has been assigned to the electronic transition $2b_2$–3p.

The third system (III) consists of a series of sharper and more closely spaced bands. Except for the first member of this series, the rest have not been assigned to Rydberg series earlier. It is observed that starting from 1134 Å (10.9 eV) down to 1100 Å (11.3 eV), the structure of the bands is sharp and regular after which the bands become broader and more irregularly spaced. These bands are assigned to the transition $6a_1$–3s. However, our analysis shows



(a)

(b)

FIGURE 2 **(a) The VUV absorption spectrum of CH_2F_2 in the spectral region 1050–1500 Å recorded at Photophysics Beamline, Indus-1; (b) Expanded view of band systems II and III of CH_2F_2 in eV scale.**

that there is an overlap between systems II and III, with bands belonging to system II continuing into system III.

Using the same sources for the values of ionization energies,[8,9] and following a similar procedure as that of Seccombe et al.[7] we have assigned all observed bands into Rydberg series. While classifying the observed transitions into Rydberg series, we found some surprising results that deviate from those of Seccombe et al. It is also observed that they have used adiabatic ionization potentials for assignment of some bands and vertical ionization potentials for other bands. We have based our calculations on the most recent high-resolution photoelectron spectroscopy data for ionization energies, viz. the work of Pradeep and Shirley.[9] The ordering of the excited electronic states followed is as per the work by Brundle et al.[8] The expected positions of the absorption bands were predicted using the standard formula for Rydberg states, viz.

$$E_n = I - \frac{R_H}{(n-\delta)^2}$$

where E_H is the energy of the transition, I is the ionization potential, R_H is the Rydberg constant, n is the principal quantum number, and δ is the quantum defect of the orbital.

Quantum defects used were those of the s and p orbitals of atomic fluorine.[17] The list of expected versus observed transitions is summarized in Table 1. It is particularly interesting to note that Pradeep and Shirley have observed three band progressions in their photoelectron spectra, and this is reflected in the observation of three band progressions in the photoabsorption spectrum. In fact, assignment of the bands in systems II and III shows that the vibrational progression beginning in system II continues well into system III. Our calculations lead us to conclude that the members of these three progressions are overlapped too strongly to be distinguishable with the experimental resolution in band system II but are well separated in band system III, a conclusion that is borne out by the fact that the relative widths of the bands are approximately in the ratio of 3:1. As can be seen from Table 1, there is a very good agreement between the calculated and observed values.

The drop in intensity between systems II and III suggests that there are indeed two different electronic transitions, as reported in earlier studies.[3,6,7] However, the higher vibrational bands of system II may be overlapping with the lower vibrational bands of system III. A high-resolution study of the VUV spectrum would be necessary to distinguish these bands clearly and explain the spectrum fully. We have also predicted the expected positions of the higher members of the Rydberg series ($n \geq 4$). Calculations for $n = 4$, 5, and 6 are listed in Table 2. As most of these transitions fall in the energy region higher than the cutoff of LiF (1050 Å), detection of these bands was beyond the scope of the current study. There is no known window material that transmits in the wavelength region below 1050 Å. Efforts have been initiated in our laboratory to

TABLE 1 **Predicted Band Positions Calculated on the Basis of Known Ionization Energies and Observed Band Positions in Electron Volt Units**

BAND SYSTEM I: ($2b_2$–3s (n = 3); $\delta = 1.16$)

Ionization energy[a]	Predicted band position	Observed band position
13.278	9.26	9.34

BAND SYSTEMS II and III: ($2b_2$–3p and $6a_1$–3s (n = 3); $\delta = 0.75$)

Progression 1			Progression 2			Progression 3		
Ionization energy	Predicted band position	Observed band position	Ionization energy	Predicted band position	Observed band position	Ionization energy	Predicted band position	Observed band position
12.729	10.04	10.03	12.729	10.04	10.03	12.729	10.04	10.03
12.872	10.19	10.18	12.874	10.19	10.18	12.859	10.18	10.18
13.010	10.32	10.32	13.014	10.33	[b]	12.989	10.30	10.30
13.195	10.51	[b]	13.152	10.47	[b]	13.118	10.43	10.45
13.278	10.59	10.58	13.289	10.60	[b]	13.247	10.56	[b]
13.407	10.72	10.71	13.435	10.75	[b]	13.375	10.69	[b]
13.535	10.85	10.84	13.560	10.87	[b]	13.502	10.82	[b]
13.660	10.97	10.99	13.694	11.01	11.04	13.628	10.94	10.94
13.780	11.09	11.09	13.827	11.14	11.14	13.753	11.07	11.07
13.898	11.21	11.25	13.959	11.27	11.29	13.877	11.19	11.19
14.013	11.33	11.34	14.090	11.40	11.40	14.001	11.32	11.31
14.127	11.44							

[a] All ionization energies are taken from Ref. 9.

[b] Not resolved in observed spectra.

TABLE 2 **Calculated Positions of Higher Members of Rydberg Series[a]**

BAND SYSTEM I: Higher Rydberg series members; $\delta = 1.16$

Ionization energy	n = 4	n = 5	n = 6
13.278	11.59	12.36	12.70

BAND SYSTEMS II and III: Higher Rydberg series members; $\delta = 0.75$

	Progression 1				Progression 2				Progression 3		
Ionization energy	Predicted absorption band position			Ionization energy	Predicted absorption band position			Ionization energy	Predicted absorption band position		
	n = 4	n = 5	n = 6		n = 4	n = 5	n = 6		n = 4	n = 5	n = 6
12.729	11.44	11.98	12.24	12.729	11.44	11.98	12.24	12.729	11.44	11.98	12.24
12.872	11.58	12.12	12.38	12.874	11.59	12.12	12.38	12.859	11.57	12.11	12.37
13.010	11.72	12.26	12.52	13.014	11.73	12.26	12.52	12.989	11.70	12.24	12.50
13.195	11.90	12.44	12.70	13.152	11.86	12.40	12.66	13.118	11.83	12.37	12.62
13.278	11.99	12.53	12.78	13.289	12.00	12.54	12.80	13.247	11.96	12.49	12.75
13.407	12.12	12.65	12.91	13.435	12.15	12.68	12.94	13.375	12.09	12.62	12.88
13.535	12.25	12.78	13.04	13.560	12.27	12.81	13.07	13.502	12.21	12.75	13.01
13.660	12.37	12.91	13.17	13.694	12.41	12.94	13.20	13.628	12.34	12.88	13.13
13.780	12.49	13.03	13.29	13.827	12.54	13.07	13.34	13.753	12.47	13.00	13.26
13.898	12.61	13.15	13.40	13.959	12.67	13.21	13.47	13.877	12.59	13.12	13.38
14.013	12.73	13.26	13.52	14.090	12.80	13.34	13.60	14.001	12.71	13.25	13.51
14.127	12.84	13.37	13.63								

[a] All values quoted are in units of electron volts.

introduce a differential pumping system between the cell and the beamline, which would enable experiments down to 500 Å. Again, the unraveling of the spectra in this region would be complex and require higher resolution due to severe overlaps between various Rydberg series members.

In band system III (i.e., in the wavelength region corresponding with about 10.9 eV to 11.5 eV), the relatively intense absorption features are due to a progression with separation of $\sim$400 cm^{-1}. However the weaker features cannot be explained by this. Our analysis indicates that progressions of band system II continue well into band system III, with a decaying intensity. These peaks are merged (within the current experimental resolution) with the band III progressions appearing at 10.94 eV, 10.99 eV, 11.04 eV, and so forth. The weaker features on the other hand, for example at 11.07 eV and 11.19 eV, are solely due to band II progressions. The strong features of band III are observed to fall into a progression with constant separation of about 403 cm^{-1} ($\pm$2 cm^{-1}). This is in agreement with Seccombe et al. However, they have mentioned only the first six members, and the error bar was of the order $\pm$60 cm^{-1}. The current study shows that at least eight members fit very well into this progression. The relatively large error bar obtained by Seccombe et al. may be due to the fact that they included some of the peaks that actually belong to the band II progression.

Ab initio calculations of $CH_2F_2^+$ have been carried out by Takeshita[12] who has reported calculated vibrational frequencies for the states $^2B_2$, $^2B_1$, $^2A_1$, and $^2A_2$. It is seen that the calculated frequencies for the ground state are in general overestimated relative to the experimental frequencies, in the case of ν_4 by about 50 cm^{-1}. As per this calculation, the ν_4 frequency in the $^2A_1$ state (479 cm^{-1}) is closest to the one observed in the current study, assuming there is an overestimation of frequency by about 80 cm^{-1}. Proposed assignments of the stronger features of band system III carried out on the basis of the foregoing discussion are tabulated in Table 3. Further *ab initio* calculations as well as experiments at higher resolution would be required to consolidate the assignments in the VUV region.

TABLE 3 **Proposed Assignments of the Strong Features of Band System III (Transition: $^1A_1$–$^2A_1$)**

Peak position (eV)	Peak position (cm^{-1})	Peak separation (cm^{-1})	Assignments
10.94	88,226		(0,0)
10.99	88,629	403	(0,1)
11.04	89,032	403	(0,2)
11.09	89,436	404	(0,3)
11.14	89,838	402	(0,4)
11.19	90,242	404	(0,5)
11.24	90,645	403	(0,6)
11.29	91,048	403	(0,7)

CONCLUSIONS

The VUV absorption spectrum of CH_2F_2 has been reinvestigated in the wavelength region 1050–1500 Å. The features observed in the current studies agree very well with previously reported work. The observed bands have been interpreted and assigned in terms of Rydberg series. Our results suggest that band system III consists of two overlapping electronic transitions, one continued from band system II starting at 1237 Å and another starting at 1190 Å. A high-resolution study that further resolves the spectral features and extension of the experiments into the windowless region would be necessary for a complete understanding.

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