

A study of molecular Rydberg transitions of monofluoroethylene and difluoroethylenes

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Molecular Rydberg transition of monofluoroethylene and difluoroethylenes has been studied employing RINDO (Rydberg Intermediate Neglect of Differential Overlap) method. Koopmans ionization potential and valence as well as Rydberg excitation band energies are calculated. These include singlet-singlet and singlet-triplet transition as well as singlet-triplet splitting energies. The results are compared with earlier theoretical and experimental results. The present singlet-triplet transitions ($\pi \rightarrow \pi^*$) energies are very close to the experimental results. Singlet-singlet transition ($\pi \rightarrow \pi^*$) also give good agreement with the experimental results.

The monofluoroethylene and difluoroethylenes [*cis*-difluoroethylene, 1,1-difluoroethylene, *trans*-difluoroethylene] have been studied by variable angle electron impact spectroscopy¹. Belanger and Sandorfy² have studied spectroscopy of the fluoroethylene series. Lake and Thompson³ have reported the photoelectron spectra of 1,1-difluoroethylene and tetrafluoroethylene. A number of other fluorinated ethylene molecules were studied by Salahub⁴. Apart from these experimental studies INDO⁵, RCNDO/S⁶, and later MRINDO/S⁷ methods have been used to study them theoretically.

Methodology

In the present study theoretical calculations have been carried out on four molecules [monofluoroethylene (mono-f.e.), *cis*-difluoroethylene (*cis*-d.f.e.), *trans*-difluoroethylene (*trans*-d.f.e.) and 1,1-difluoroethylene (1,1-d.f.e.)]. Only two of the above fluorinated ethylenes (mono-f.e. and *cis*-d.f.e.) were studied earlier using MRINDO/S⁷ scheme but all the four were studied using INDO⁵ scheme. RINDO scheme can be used to interpret molecular Rydberg transitions, but INDO can not be used for this purpose. Further, methodology based on screening of π -orbitals leads to smaller π -MO (molecular orbital) values in comparison to the values given by the unscreened schemes. Secondly, in the case involving screening of orbitals, it is found that the calculated values for singlet and triplet $\pi \rightarrow \pi^*$ transition energies are smaller as compared to the experimental results for fluoroethylenes. Thus, in the present calculation the

RINDO method has been used to obtain better values of singlet and triplet $\pi \rightarrow \pi^*$ transition energies as well as corresponding splitting by neglecting screening of π -orbitals. The effect of unscreened π -MOs on Rydberg states and corresponding transitions of all concerned molecules has also been studied. The present calculations have been carried out under limited CI treatment and only thirty singly excited configurations have been considered for both singlet and triplet states. These, however, take care of electron correlation to some extent. For the sake of comparison of present results with the results obtained using MRINDO/S and RCNDO/S schemes, convergence criteria have been taken with 0.0001 and 0.001 a.u. for Jacobi diagonalization and SCF procedure respectively as in the case of the MRINDO/S and RCNDO/S schemes. The bonding parameters are taken as 0.42 for valence interactions and 0.045 for Rydberg interactions.

Results and Discussion

Ground state

The vertical ionization potentials have been calculated using Koopmans theorem. The values are shown along with experimental^{1,8} IP's in Table 1. The calculated IPs are slightly higher for π -MOs compared to values calculated by MRINDO/S⁷ method as well as experimental values. The values of valence π -MOs calculated by RINDO method are found higher than those calculated by MRINDO/S method. the same is the case for Rydberg MOs. However, increase in the latter case is greater. It has been established that the most easily

Table 1—The five lowest ionization potentials of fluoroethylenes (eV)

Molecule	Exptl.	RINDO/S		% error in estimation
	IP	IP	Sym.	
CH ₂ = CHF (C _s)	10.58 ⁸	11.78	A''(π)	11.34
		13.66	A'(σ)	
		15.25	A'(σ)	
		17.16	A'(σ)	
		17.39	A''(π)	
FHC = FHC (C _{2v}) (cis)	10.43 ¹	11.53	B ₁ (π)	10.54
		13.79	A ₁ (σ)	
		15.50	B ₂ (σ)	
		16.98	A ₁ (σ)	
		17.09	B ₁ (π)	
H ₂ C = CF ₂ (C _{2v})	10.72 ¹	11.78	B ₁ (π)	09.89
		14.97	A ₁ (σ)	
		16.05	B ₂ (σ)	
		16.36	A ₁ (σ)	
		16.92	B ₁ (π)	
CHF = CHF (C ₂) (trans)	10.38 ¹	11.60	A(π)	11.75
		13.77	B(σ)	
		16.24	B(σ)	
		16.60	B(σ)	
		17.50	A(π)	

removable electron in both monofluoroethylene and difluoroethylenes is the C=C π-electron as was the case in MRINDO/S method. The order of lowest IPs, which are associated with π-MO, is: *cis*-d.f.e. < *trans*-d.f.e. < mono-f.e. = 1,1-d.f.e. However the experimental results show the trend: *trans*-d.f.e. < *cis*-d.f.e. < *mono*-f.e. < 1,1-d.f.e. Thus, the trend of IP values is not in accordance with the experimental results. Even then, values of IPs are reasonably close to the corresponding experimental results^{1,8}.

The substitution of fluorine for hydrogen in planar molecules has much larger stabilizing effect on the σ-MOs than that on the π-MOs. This is due to the so-called perfluoro effect⁹. In the present work this effect is well accounted for in the cases of second and third IPs which are associated with the σ-MOs. On the basis of earlier calculated^{10,11} results, one may easily conclude that the substitution of fluorine in place of hydrogen in planar molecules has much larger stabilizing effect on the σ-MOs than that on the π-MOs. Because of the high electronegativity of the fluorine, the electron densities on the bond in such compounds tends towards the F atom where 2*p* orbitals are less affected by the successive fluorination. This is

because 2*p* orbitals are perpendicular to the plane of the molecule and their charge densities remain almost constant while planar σ-electron framework is highly affected by the fluorination. Accordingly, occupied σ-MOs of difluoroethylenes are more stabilized than those of the monofluoroethylene. Moreover, second and third IP values of fluorinated ethylenes are found closer to the experimental results as compared to those obtained using MRINDO/S scheme.

Order of calculated second IP's is as follows: mono-f.e. < *trans*-d.f.e. < *cis*-d.f.e. < 1,1-d.f.e.

Excitations

Results of S → S transitions are given in Table 2 and those of S → T transitions and S → T splitting are given in Table 3.

Brundle *et al.*¹² suggested that effect of fluorination in ethylene is to depress the occupied σ-MO manifold compared to π-MO manifold. This explanation has been given for tri- and tetra-fluoroethylenes. However, in the present investigation the same effect is observed for monofluoroethylene where energies of lowest occupied π-MOs of monofluoroethylene and difluoroethylenes are found to be equal (11.78 eV).

As per the fluorination effect, the π → σ* transition energy should be small as compared to π → π* transition energy. But in the present work, due to the neglect of the effect of screening on π-MOs, considerably higher values are obtained for π-MOs and π → π* energies than those obtained using the screened MRINDO scheme. Thus π → σ*, σ → σ* and σ → π* bands are followed by π → π* band.

The π → π* transitions of fluoroethylenes exhibit higher intensities than those predicted by the MRINDO/S scheme which are in the 7.9-9.1 eV region. O'Malley and Jennings⁸ found the singlet π → π* transitions centred at 58000 cm⁻¹ (~7.19 eV). Due to the neglect of the effect of screening on π-orbitals the singlet π → π* transition energies are found to be somewhat higher than the experimental results, but these show better agreement with the experimental results than that shown by the results obtained by the MRINDO/S scheme. It is established that the π → π* band energy decreases as fluorination increases. Present results show the following trend in π → π* band energies: mono-f.e. > *trans*-d.f.e.

The above mentioned decrease is not seen in the case of 1,1-d.f.e. and *cis*-d.f.e. It may be due to higher values of virtual π-MOs calculated for 1,1-d.f.e. and *cis*-d.f.e. The oscillator strengths for π → π* transitions have been calculated to be 0.14,

0.19, 0.27 and 0.37 for mono-f.e., *trans*-d.f.e., *cis*-d.f.e. and 1,1-d.f.e. respectively, which are not found to be constant as also observed in the case of calculation by MRINDO/S scheme. However, the highest intensity is observed for 1,1-d.f.e. which is in agreement with the experimental results.

The highest intensity $\sigma \rightarrow \sigma^*$ band of fluoroethylenes appears in the 6.10-9.65 eV region. Thus, the near constancy of the $\sigma \rightarrow \sigma^*$ band is well accounted for mono-f.e., *cis*-d.f.e. and 1,1-d.f.e. Moreover, the present work shows better near constancy of the $\sigma \rightarrow \sigma^*$ band energies ($\Delta E = 9.40, 9.35$ eV) for mono-f.e. and *cis*-d.f.e. than that ob-

Table 2—The S→S transitions of fluoroethylenes (eV)

Molecule	Exptl.		RINDO		% Rydberg character				
	ΔE	ΔE	f	Sym.	H	C	F	T	
H ₂ C = CHF (C _s)	7.44 ^N	5.07	0.00	A'' ($\pi \rightarrow \sigma^*$)	1	1	0	2	
		6.81	0.006	A' ($\pi \rightarrow \sigma^*$)	1	1	0	2	
		7.34	0.00	A'' ($\pi \rightarrow \sigma^*$)	9	14	0	23	
		7.89	0.00	A'' ($\sigma \rightarrow \pi^*$)	1	1	0	2	
		8.10	0.14	A' ($\pi \rightarrow \pi^*$)	2	2	0	4	
		8.84	0.00	A'' ($\pi \rightarrow \sigma_R^*$)	34	44	1	79	
		9.39	0.00	A' ($\pi \rightarrow \sigma_R^*$)	29	65	1	95	
		9.40	0.10	A' ($\sigma \rightarrow \sigma^*$)	9	15	0	24	
		9.42	0.02	A' ($\pi \rightarrow \sigma_R^*$)	28	50	1	79	
		9.46	0.00	A'' ($\pi \rightarrow \sigma_R^*$)	32	64	1	97	
		9.67	0.00	A'' ($\sigma \rightarrow \pi^*$)	4	29	0	33	
		9.68	0.00	A'' ($\pi \rightarrow \pi_R^*$)	7	62	0	69	
		10.13	0.00	A'' ($\pi \rightarrow \sigma_R^*$)	53	42	0	95	
		10.16	0.00	A' ($\pi \rightarrow \sigma_R^*$)	22	65	0	87	
		10.21	0.00	A' ($\pi \rightarrow \sigma_R^*$)	19	80	0	99	
		10.29	0.00	A'' ($\pi \rightarrow \sigma^*$)	3	8	0	11	
		10.50	0.00	A' ($\pi \rightarrow \sigma_{RV}^*$)	30	16	1	47	
10.59	0.07	A' ($\sigma \rightarrow \sigma^*$)	6	13	0	19			
FHC = CHF (C _{2v}) (<i>cis</i>)	6.49 ^N	4.45	0.00	B ₁ ($\pi \rightarrow \sigma^*$)	0	0	0	0	
		7.81 ^N	5.20	0.00	A ₂ ($\pi \rightarrow \sigma^*$)	1	1	0	2
FCH = FCH (C _{2v})	6.49 ^N	6.44	0.003	A ₁ ($\sigma \rightarrow \sigma^*$)	0	0	0	0	
		7.81 ^N	7.32	0.00	B ₂ ($\sigma \rightarrow \sigma^*$)	1	0	0	1
		7.90	0.00	B ₁ ($\sigma \rightarrow \pi^*$)	1	0	0	1	
		7.94	0.00	B ₁ ($\pi \rightarrow \sigma_R^*$)	39	22	1	62	
		8.34	0.27	A ₁ ($\pi \rightarrow \pi^*$)	1	0	0	1	
		8.40	0.00	B ₁ ($\pi \rightarrow \sigma_R^*$)	21	71	4	96	
		9.03	0.00	B ₁ ($\pi \rightarrow \sigma_R^*$)	33	64	3	100	
		9.06	0.00	A ₂ ($\pi \rightarrow \sigma_R^*$)	29	65	2	96	
		9.29	0.00	B ₁ ($\pi \rightarrow \sigma_R^*$)	9	90	0	99	
		9.35	0.09	B ₂ ($\sigma \rightarrow \sigma^*$)	0	0	0	0	
		9.52	0.00	A ₂ ($\pi \rightarrow \sigma^*$)	6	9	0	15	
		9.75	0.00	B ₁ ($\pi \rightarrow \sigma_R^*$)	46	35	0	81	
		9.81	0.00	A ₁ ($\pi \rightarrow \sigma_R^*$)	25	75	0	100	
		9.81	0.00	A ₂ ($\pi \rightarrow \sigma_R^*$)	24	64	0	88	
		9.83	0.00	A ₂ ($\sigma \rightarrow \sigma^*$)	1	1	0	2	
10.17	0.00	B ₁ ($\pi \rightarrow \sigma^*$)	10	6	0	16			
H ₂ C = CF ₂ (C _{2v})	6.95 ^l	4.17	0.00	B ₁ ($\pi \rightarrow \sigma^*$)	0	0	0	0	
		6.74	0.007	A ₁ ($\sigma \rightarrow \sigma^*$)	0	0	0	0	
		7.19	0.00	A ₂ ($\pi \rightarrow \sigma^*$)	12	16	1	29	
		7.29	0.00	B ₁ ($\pi \rightarrow \sigma^*$)	5	11	1	17	

(*contd.*)

Table 2—The S → S transitions of fluoroethylenes (eV)—Contd.

Molecule	Exptl.		RINDO		% Rydberg character			
	ΔE	ΔE	f	Sym.	H	C	F	T
H ₂ C = CF ₂ (C _{2v})	6.95 ¹	8.59	0.00	A ₁ (σ → σ*)	0	0	0	0
		8.60	0.00	B ₁ (π → σ _R [*])	15	69	4	88
		8.85	0.00	B ₁ (π → σ*)	0	1	0	1
		9.03	0.00	B ₁ (σ → π*)	1	0	0	1
		9.11	0.37	A ₁ (π → π*)	6	14	1	21
		9.24	0.00	B ₁ (π → σ _R [*])	25	72	2	98
		9.26	0.00	A ₂ (π → σ _{Rv} [*])	22	53	2	57
		9.28	0.10	A ₁ (π → π _R [*])	25	54	2	81
		9.51	0.00	B ₁ (π → π _R [*])	9	91	0	100
		9.65	0.20	B ₂ (σ → σ*)	0	0	0	0
		9.98	0.00	B ₁ (π → σ _R [*])	53	45	1	99
		10.00	0.00	A ₂ (π → σ _R [*])	13	79	0	92
		10.05	0.00	A ₁ (π → π _R [*])	19	80	0	99
		10.33	0.00	A ₂ (π → σ*)	15	5	0	20
FHC = CHF (C ₂) (trans)	- 6.64 ⁸	3.84	0.00	A(π → σ*)	0	1	0	0
		6.10	0.004	B(σ → σ*)	0	0	0	0
		6.50	0.00	A(π → σ _{Rv} [*])	7	36	2	45
		7.17	0.00	B(π → σ*)	8	28	1	37
		7.77	0.00	B(σ → σ*)	2	10	1	13
		7.85	0.00	B(σ → π*)	1	0	0	1
FHC = CHF (C ₂)	6.64 ⁸	7.90	0.19	A(π → π*)	1	2	0	3
		8.45	0.00	A(π → σ _{Rv} [*])	7	43	3	53
		9.06	0.00	B(π → σ _R [*])	14	64	3	81
		9.11	0.00	A(π → σ _R [*])	22	75	3	100
		9.16	0.00	B(π → σ _R [*])	15	69	1	85
		9.36	0.00	A(π → σ _R [*])	7	92	0	99
		9.56	0.00	A(π → σ*)	2	8	2	12
		9.83	0.00	B(π → σ _R [*])	38	59	1	98
		9.85	0.00	B(π → π _R [*])	6	82	0	88
		9.89	0.00	A(π → π _R [*])	3	97	0	100
		10.04	0.00	B(σ → σ*)	6	29	2	37
10.20	0.00	B(π → σ*)	3	9	4	16		

tained using the MRINDO/S scheme. In the same case σ → σ* band energies decrease as fluorination increases. The σ → σ* band is found to be intense for fluoroethylenes except for the *trans*-d.f.e. (f=0). Further, in earlier work⁷, the valence σ → σ* band was not found for ethylene. It may be due to the fact that more and more of Rydberg excitation region is occupied by the σ → σ* band as fluorination decreases. Accordingly, in the present study the per cent Rydberg characters of the σ → σ* band for mono-f.e., *cis*-d.f.e., *trans*-d.f.e. and 1,1-d.f.e. are found to be 24, 0, 0 and 13 respectively. Thus, the absence of the σ → σ* valence band in ethylene could be explained by the present results.

In the case of highest π-MO ionization potentials, near constancy is observed and it causes

near constancy of π → 3s and π → 3p absorption energy. Thus, one can easily assume that the Rydberg transitions are terminating at 3s and 3p.

The first Rydberg transition is assigned as π → σ_R^{*} which appears at energies 8.84, 7.94, 6.50 and 8.60 eV for mono-f.e., *cis*-d.f.e., *trans*-d.f.e. and 1,1-d.f.e. respectively. The corresponding quantum defects (δ) are 0.85, 1.05, 1.37 and 0.93. Thus, the first Rydberg transition corresponds to π → 3s excitation. Similarly, the second Rydberg transition for mono-f.e., *cis*-d.f.e., *trans*-d.f.e. and 1,1-d.f.e. appears at 9.39, 8.40, 8.45 and 9.24 eV with corresponding (δ) values as 0.61, 0.92, 0.92 and 0.69 respectively. These transitions again correspond to π → 3s. Thus, the near constancy for π → 3s excitation is observed. In the present investigation the π → 3s excitations in flu-

Table 3—The S→T transition energies of fluoroethylenes (eV)

Molecule	RINDO			% Rydberg character			
	ΔE	S→T split	Sym.	H	C	F	T
H ₂ C=CHF (C _s)	4.02	1.05	A''($\pi \rightarrow \sigma^*$)	0	0	0	0
	4.56	3.54	A'($\pi \rightarrow \pi^*$)	1	0	0	1
	6.02	0.79	A'($\sigma \rightarrow \sigma^*$)	1	1	0	2
	7.61	0.28	A''($\sigma \rightarrow \pi^*$)	1	0	0	1
	8.80	0.04	A''($\pi \rightarrow \sigma_R^*$)	23	59	2	84
CHF=CHF (C _{2v}) (<i>cis</i>)	3.35	1.10	B ₁ ($\pi \rightarrow \sigma^*$)	0	0	0	0
	4.24	4.10	A ₁ ($\pi \rightarrow \pi^*$)	1	0	0	1
	5.90	0.54	A ₁ ($\sigma \rightarrow \sigma^*$)	0	0	0	0
	7.62	0.32	B ₁ ($\pi \rightarrow \sigma_R^*$)	41	20	1	62
	7.66	0.24	B ₁ ($\sigma \rightarrow \pi^*$)	1	0	0	1
H ₂ C=CF ₂ (C _{2v})	3.13	1.04	B ₁ ($\pi \rightarrow \sigma^*$)	0	0	0	0
	4.55	4.56	A ₁ ($\pi \rightarrow \pi^*$)	1	1	0	2
	6.40	0.34	A ₁ ($\sigma \rightarrow \sigma^*$)	0	0	0	0
	6.40	0.89	B ₁ ($\pi \rightarrow \sigma^*$)	5	11	1	17
	8.74	0.29	B ₁ ($\sigma \rightarrow \pi^*$)	1	1	0	2
CHF=CHF (C ₂) (<i>trans</i>)	2.76	1.08	A($\pi \rightarrow \sigma^*$)	0	0	0	0
	4.29	3.61	A($\pi \rightarrow \pi^*$)	0	0	0	0
	5.42	0.68	B($\sigma \rightarrow \sigma^*$)	0	0	0	0
	5.86	0.64	A($\pi \rightarrow \sigma_{RV}^*$)	7	36	2	45
	7.62	0.23	B($\sigma \rightarrow \pi^*$)	1	0	0	1

orinated ethylenes appear in the 6.50-9.39 eV region. The same $\pi \rightarrow 3s$ excitation energies were calculated in the region 6.2-6.7 eV by Brundle *et al.*¹² and the observed experimental values are 6.97 and 6.49 eV for mono-f.e. and *cis*-d.f.e. respectively⁸. Present values of $\pi \rightarrow 3s$ excitation are found to be somewhat higher than the experimental values. This may be due to higher IPs calculated for the fluorinated ethylenes. However, present calculated values of $\pi \rightarrow 3s$ excitation energies of *cis*-d.f.e. are found closer to the experimental values and gaussian orbital calculation¹² than those obtained using the MRINDO/S scheme. Moreover, the first $\pi \rightarrow 3s$ excitation of *trans*-d.f.e. is observed to be very close to the gaussian orbital calculations.

The third Rydberg excitation in mono-f.e., *cis*-d.f.e., *trans*-d.f.e. and 1,1-d.f.e. appears at 9.42, 9.03, 9.06 and 9.28 eV with the quantum defects 0.60, 0.67, 0.69 and 0.67 respectively. Values of δ very clearly show that the third Rydberg excitation corresponds to $\pi \rightarrow 3p$. Again, greater near constancy is observed for excitation energies and quantum defects than that in the MRINDO/S scheme. Calculated energy values fall well within the experimental region of 65000 cm⁻¹ (~8.1 eV)⁸.

The region of $\pi \rightarrow 3d$ excitations lies above 9.0 eV; but, in the present work Rydberg *d* atomic orbitals (AOs) are not included in the basis set.

The S→T ($\pi \rightarrow \pi^*$) transition energies of mono-f.e., *cis*-d.f.e., *trans*-d.f.e. and 1,1-d.f.e. are found to be 4.56, 4.24, 4.29 and 4.55 eV respectively whereas the experimental values are 4.40, 4.43, 4.18 and 4.63 eV respectively. Thus, the present results fall well within the range of experimental results.

The calculated singlet $\pi \rightarrow \pi^*$ transitions and triplet $\pi \rightarrow \pi^*$ transitions lie in the ranges 7.90-9.11 eV and 4.10-4.54 eV respectively. O'Malley and Jennings¹³ found the singlet and triplet $\pi \rightarrow \pi^*$ transitions centered at 58000 cm⁻¹ (7.19 eV) and 35400 cm⁻¹ (4.37 eV) respectively. The triplet transition energies lie very near to the experimental^{1,13} values, but due to use of high calculated IPs for the series and neglect of screening of π -MOs, the singlet $\pi \rightarrow \pi^*$ transition energies are somewhat higher. These larger values of singlet $\pi \rightarrow \pi^*$ transition energies lead to the splitting value being higher by 0.7 eV to 1.75 eV as compared to the experimental^{1,13} splitting values.

In the study of variable angle electron impact spectroscopy¹, the Rydberg S→T transition is observed with low intensity for only *cis*-d.f.e. at about 6.4 eV. It could be the S→T ($\pi \rightarrow \sigma_R^*$) transition associated with S→S ($\pi \rightarrow \sigma_R^*$) at 7.0¹ eV. Moreover, they have detected no analogous Rydberg S→T transitions in mono-f.e., *trans*-d.f.e. and 1,1-d.f.e. Presumably, it may be due to overlapping of the S→T ($\pi \rightarrow \sigma_R^*$) in mono-f.e., *trans*-

d.f.e. and 1,1-d.f.e. with nearby intense S→T transition. But, in the present study, the S→T ($\pi \rightarrow \sigma_R^*$) transitions of mono-f.e. and *cis*-d.f.e. are observed at 8.80 and 7.62 eV respectively, where respective per cent Rydberg character is 84 and 62. Secondly, for the case of *trans*-d.f.e. the triplet mixed (valence and Rydberg) $\pi \rightarrow \sigma^*$ transition is obtained at 5.86 eV, where the per cent Rydberg character is 45. The S→T ($\pi \rightarrow \sigma_R^*$) transition is not found in 1,1-d.f.e. (Table 3).

The S→T $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ splittings of fluoroethylenes are found in the ranges 0.34-0.79 eV, 1.04-1.10 eV and 0.23-0.29 eV respectively and thus the near constancy is observed.

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References

- 1 Kuppermann A, Flincker W M & Mosher O A, *Chem Rev*, 79 (1979) 180.
- 2 Belanger G & Sandorfy C, *Chem Phys Lett*, 3 (1969) 661; *J chem Phys*, 55 (1971) 2055.
- 3 Lake R F & Thompson H, *Proc Roy Soc London*, A315 (1970) 323.
- 4 Salahub D E, *Theoret chim Acta*, 22 (1971) 330.
- 5 Jha R & Singh A N, *Indian J Phys*, 53B (1979) 117.
- 6 Prasad R S & Singh A N, *Indian J Phys*, 56B (1982) 35.
- 7 Prasad R S & Sharma R, *Indian J Phys*, 61B (1987) 87.
- 8 Robin M B, *Higher excited states of polyatomic molecules*, (Academic Press, NY) 1975.
- 9 Brundle C R & Robin M B, in *Determination of organic structures by physical method*, Vol. III edited by F Nachod & G Zuckerman (Academic Press, NY), 1971.
- 10 Barfield M & Johnston M D, *Chem Rev*, 73 (1973) 67.
- 11 Liebman J F & Greenberg A, *Chem Rev*, 76 (1976) 344.
- 12 Brundle C R, Robin M B, Kuebler N A & Basch H, *J Am chem Soc*, 94 (1972) 1451.
- 13 O'Malley R M & Jenning K R, *J mass spectrum Ion Phys*, 2 (1969) App 1.