Theoret. chim. Acta (Berl.) 22, 325–329 (1971)

Semi-Empirical MO–CI Calculations on Excited States

III. Saturated Molecules*

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Received December 2, 1970

Results of semi-empirical MO–CI calculations of the INDO and RCNDO type are presented for the electronic spectra of some amines, the fluoromethanes, and some perfluoroalkanes. Reasonable assignments for the lower electronic bands are found in the large majority of cases.

Die Ergebnisse semiempirischer MO–CI-Rechnungen vom INDO- und RCNDO-Typ für die Elektronenspektren einiger Amine, des Fluormethans und einiger Perfluoralkane werden mitgeteilt. Für die größte Zahl der Moleküle können die niedrigeren elektronischen Übergänge gedeutet werden.

On présente les résultats de calculs semi-empiriques MO–CI du type INDO et RCNDO pour les spectres électroniques de quelques amines, les fluorométhanes, et quelques alcanes perfluorées. Des attributions raisonnables sont données pour les bandes électroniques de plus basse énergie dans la plupart des cas.

Introduction

In previous publications [1, 2] we have described semi-empirical MO–CI methods which we found useful in the interpretation of the electronic spectra of alkanes [1] and alcohols and fluoroalcohols [2]. The most extensive of these methods, RCNDO, included atomic Rydberg orbitals in the basis set.

We have applied these methods to a large number of simple molecules containing H, C, N, O, and F. The necessary bonding parameters for the INDO method are shown in Table 1. The "average" ionization potentials for the Rydberg orbitals are shown in Table 2. Experimental geometries were used when available, otherwise reasonable values for bond-lengths and angles were assumed from related molecules.

Table 1. *Bonding parameters* (eV) *for the* INDO *method*

A–B	H–H	H–C	H–N	H–O	H–F	C–C
$-\beta^{\circ}_{A-B}$ (eV)	9.5	11.0	13.8	17.5	5.0	15.0
	C–N	C–O	C–F	O–F	F–F	
	22.0	24.0	32.0	40.0	60.0	

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* Paper I: Salahub, D. R., Sandorfy, C.: Theoret. chim. Acta (Berl.) **20**, 227 (1971).
Paper II: Salahub, D. R., Sandorfy, C.: Chem. Physics Letters **8**, 71 (1971).

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Table 2. "*Average*" *ionization potentials* (eV) *for Rydberg orbitals*

Atom	H		C		N		O		F	
Orbital	$2s$	$2p$	$3s$	$3p$	$3s$	$3p$	$3s$	$3p$	$3s$	$3p$
I (eV)	3.399	3.399	3.735	2.509	4.329	3.144	4.378	3.053	6.191	4.579

In this paper we present results for some amines, the fluoromethanes, and some perfluoroalkanes. Because of the relatively large number of molecules studied, we give only the principal results related to electronic transitions. More extensive results, including charge distributions, lone-pair delocalization, ionization potentials, and singlet-singlet and singlet-triplet transitions are available on request, in the form of technical reports.

Results and Discussion

Amines

We have studied ammonia in the INDO and RCNDO approximations and ammonia, methyl-, dimethyl-, trimethyl-, and ethylamine by the INDO method only. The relatively large amount of computer time required for the extended basis set calculations led us to try and obtain reasonable assignments using the minimum set, since this was usually possible, at least for the first few transitions, for the n-alkanes [1]. It must be kept in mind, however, that transitions to states whose wave functions contain a large contribution from excited atomic orbitals may, and are indeed expected to, fall in the same spectral region[1]. Special caution must be exercized for highly branched molecules as our results for the branched alkanes showed [1].

The results for the two lowest transitions are shown in Table 3. The first two excited states of ammonia are found to be of the $\sigma^* \leftarrow n$ type and of symmetries A_1 and E (under C_{3v}). These are consistent with the results of Douglas [4] who concluded from the study of the high resolution spectrum and the Zeeman effect, that the first excited state was non-degenerate while the second was very likely degenerate.

The first highly Rydberg transitions are found somewhat too high in the RCNDO method, mainly because of a similar overestimation of the lone-pair ionization potential. They are found at 10.17 eV ($3s \leftarrow n(\delta = 1.00)$) and 10.64 eV ($3p(e) \leftarrow n(\delta = 0.85)$).

(The inclusion of all doubly excited configurations in the INDO calculation was found to make no qualitative changes in the spectral predictions [5].)

For the amines the first transition is also found to involve excitation of a (delocalized) lone-pair electron. Our calculated results give a better mapping of the frequencies and intensities in the series [3] if we make the first calculated transition of tri-methyl amine correspond to the second observed band, provisionally assigning the first band as $R \leftarrow n$ by analogy with the assignment in iso-butane [1] which is iso-electronic with and of similar topology to trimethylamine.

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[1] We have not used the concept of united-atom Rydberg orbitals. See Ref. [1].

Table 3. *The two lowest electronic transitions of amines* (eV)

Molecule	$\Delta E_{\max}$ (expt.)[a]	f	ΔE (INDO)	f	Sym.	Type
NH_3 (C_{3v})	6.38	0.079	5.94	0.004	$A_1 \leftarrow A_1$	$\sigma^* \leftarrow n$
	8.18	0.0095	8.41	0.056	$E \leftarrow A_1$	$\sigma^* \leftarrow n$
CH_3NH_2 (C_s)	5.76	0.017	5.72	0.020	$A' \leftarrow A'$	$\sigma^* \leftarrow n$
	7.13	0.084	6.23	0.052	$A' \leftarrow A'$	$\sigma^* \leftarrow n$
$(CH_3)_2NH$ (C_s)	(5.58)	(0.0017)	—	—	—	—
	6.51	0.10	5.77	0.048	$A' \leftarrow A'$	$\sigma^* \leftarrow n$
			5.99	0.050	$A' \leftarrow A'$	$\sigma^* \leftarrow n$
$(CH_3)_3N$ (C_{3v})	5.45	0.016	—	—	—	—
	6.23	0.13	5.64	0.070	$A_1 \leftarrow A_1$	$\sigma^* \leftarrow n$
			6.03	0.006	$E \leftarrow A_1$	$\sigma^* \leftarrow n$
$C_2H_5NH_2$ (C_s)	5.83	0.019	5.69	0.052	$A' \leftarrow A'$	$\sigma^* \leftarrow n$
	7.00	0.050	6.30	0.074	$A' \leftarrow A'$	$\sigma^* \leftarrow n$

[a] Experimental values are from Ref. [3].

Our calculations predict a shift to higher energy and an increase in intensity for the first band of dimethylamine with respect to that of methylamine. Tannenbaum, Coffin, and Harrison [3] find the opposite, the first band being slightly red-shifted and weaker by a factor of ten. Our results correlate better with the second reported band so that we prefer to leave the first band unassigned at the present time. Experimental verification of its presence with a highly pure sample would be desirable.

For all the amines we find at least two additional $\sigma^* \leftarrow n$ transitions before the onset of $\sigma^* \leftarrow \sigma$ absorption.

Fluoromethanes

The spectra of CH_4, CH_3F, CH_2F_2, CHF_3, and CF_4 were presented by Edwards and Raymonda ([6] and Refs. therein). They discussed them in terms of a bond-exciton model. The experimental band maxima and INDO calculated transition energies for the first band are shown in Table 4.

The gross trends in the series are reasonably well accounted for by the calculations although the red-shift from methane to CH_3F is over-estimated and a blue-shift rather than a very small red shift is found between CH_3F and CH_2F_2. There is then a large hypsochromic shift on going to CHF_3 and another on replacing the last hydrogen which are well accounted for by our calculations. These shifts parallel those of the first ionization potentials ([7] and Refs. therein) and so are at least partly due to tighter binding in the ground state in the series

$$CH_2F_2 \rightarrow CH_3F \rightarrow CHF_3 \rightarrow CF_4 .$$

For all the partially fluorinated molecules the first transition is found to depart from an orbital which is bonding in the C–H, and π^* type anti-bonding in the C–F bonds. This is in line with recent non-empirical calculations on the

Table 4. *The lowest electronic transitions of fluoromethanes* (eV)

Molecule	$\Delta E_{\max}$ (expt.)[a]	ΔE (INDO)	Sym.
$CH_4(T_d)$	9.71	10.41	$T_2 \leftarrow A_1$
$CH_3F(C_{3v})$	9.42	8.91	$E \leftarrow A_1$
$CH_2F_2(C_{2v})$	9.35	9.45	$B_1 \leftarrow A_1$
$CHF_3(C_{3v})$	10.82	12.58	$A_1 \leftarrow A_1$
		12.81	$E \leftarrow A_1$
$CF_4(T_d)$	13.0	13.55	$T_2 \leftarrow A_1$
		13.56	$T_1 \leftarrow A_1$

[a] Experimental values are from Ref. [6].

ground states of these molecules [7]. Transitions involving lone-pair electrons on the fluorines or electrons in C–F bonds come only at higher energies.

There has been considerable discussion recently about the order of the two highest occupied (t_2 and t_1) levels of CF_4 [7–12]. The order of these levels depends upon the method of calculation. Non-empirical calculations and the available experimental results favour t_1 above t_2, whereas semi-empirical calculations predict the reverse order. In all cases the calculated separation is less than that observed.

We find the first two transitions, which depart from the t_2 and t_1 levels respectively, to be nearly degenerate. Only that departing from t_2 ($T_2 \leftarrow A_1$) is optically allowed. The t_2 orbital is found to be almost completely localized on the fluorine atoms, the carbon orbitals accounting for less than 2% of the total population. Brundle, Robin, and Basch [7] calculated an overlap population of 0.026 for the C–F bonds in this orbital, which may be compared with their value of 0.192 for the C–H bond in the t_2 orbital of methane. The highest occupied orbital with a significant population on the carbon has an orbital energy of -23.28 eV and does not figure in the thirty lowest transitions.

Perfluoralkanes

The spectra of the perfluoralkanes up to C_6F_{14} were recently reported by Bélanger, Sauvageau, and Sandorfy [13]. Their main observations were

i) a general bathochromic shift with respect to the spectra of the corresponding alkanes;

ii) a decrease in intensity with respect to these same spectra;

iii) a bathochromic shift and an increase in intensity within the series as the length of the carbon chain increases, similar to, but more accentuated than that observed for the alkanes.

Variation of the bonding parameters: β^0_{H-F}, β^0_{C-F}, and β^0_{F-F} did not allow us to account for these features so that, barring more drastic modifications of the method we were obliged to use a different $\beta^0_{C-C}(=-23\text{ eV})$ for these molecules. This may possibly be linked to observed anomalies for the ionization potential and electronegativity of fluorine (see Politzer [14] and Bykov [15]).

With this parameter, the above trends are successfully interpreted by the INDO method for CF_4, C_2F_6, and C_3F_8, for which we find first transitions at

13.55, 11.38, and 10.60 eV respectively, which may be compared with the experimental band maxima of 13.0 [6], > 11 [13], and 10.42 eV [13].

The first transitions are found to depart from MO's localized mainly in the C–C bonds, in contrast to the case of C_2H_6 and C_3H_8 where excitation is from C–H bonding orbitals [1]. The bathochromic shift is attributed mainly to hyperconjugation involving *p* orbitals in the C–C skeletal plane.

Acknowledgements. The author expresses his thanks to Professor C. Sandorfy who sponsored this research and read the manuscript.

The calculations were performed at the Centre de Calcul de l'Université de Montréal, the staff of which, we thank for their co-operation. The award of a 1967 Science Scholarship from the National Research Council of Canada is gratefully acknowledged.

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