Theoret. Chim. Acta (Berl.) 44, 245–256 (1977)

THEORETICA CHIMICA ACTA

An *ab initio* Investigation into the S_N2 Reaction: Frontside Attack versus Backside Attack in the Reaction of F^- with CH_3F

H. Bernhard Schlegel and Kurt Mislow*

Department of Chemistry, Princeton University, Princeton, N.J. 08540, USA

Fernando Bernardi and Andrea Bottoni

Laboratorio CNR Composti del Carbonio, Istituto di Chimica Organica, Viale Risorgimento 4, Università di Bologna, Bologna, Italy

The energy hypersurface for the attack of fluoride ion on methyl fluoride has been explored with *ab initio* LCAO-SCF calculations at a split-valence basis set level. Transition states for frontside and backside attack have been located. In addition to transition states, two possible F^--CH_3F clusters have been identified. The transition state for the substitution of fluoride with retention of configuration is found to be 56 kcal/mol higher than the transition state for inversion of configuration. The transition state for hydride displacement with inversion is 62 kcal/mol above the transition state for fluoride substitution with inversion.

Key words: S_N2 reaction, frontside versus backside attack - $CH_3F_2^-$ - Geometry optimization, force method

1. Introduction

The bimolecular nucleophilic substitution (S_N2) reaction is central to organic chemistry, and its energetics and stereochemistry have been the subject of extensive experimental investigations[1]. Without known exception, the S_N2 reaction at carbon centers proceeds with inversion of configuration.

With advances in computational capabilities, theoretical examinations of the S_N2 reaction have become increasingly feasible[2]. For a number of representative examples, high quality *ab initio* calculations already exist [2–14]. *A priori*, a theoretical investigation should consider all possible directions of attack by the nucleophile. These paths can be broadly divided into the two categories of frontside and backside attack. For the latter, the path of the approaching nucleophile lies within the trigonal pyramid formed by the central atom and the three non-participating substituents; this trajectory invariably leads to the familiar Walden inversion[1]. On the other hand, frontside trajec-

---

* Correspondence should be directed to this author

[1] For an authoritative account, see Ingold [1].

[2] A review of theoretical investigations of the S_N2 reaction has recently been provided by Bader and Gangi [2].

tories can, at least in principle, lead to displacement with retention. Since this stereochemical course is never observed for S_N2 displacements at carbon, the cost in energy for this approach is presumably relatively high.

The simplest theoretical model for the S_N2 reaction, $CH_4 + H^-$, has received the most attention [3–5, 8, 9, 12–14]. Details of the minimum energy pathway involving backside attack are well documented [5, 8, 9], and most theoretical investigations on larger systems, such as $CH_3X + Y^-$ (X, Y = F, Cl, CN) [6–13] and NH_3F_2 [41], have also been restricted to backside attack. Aside from certain semi-empirical studies [15–17], comparatively little is known about frontside attack for systems other than CH_5^- [3, 4, 38]. To fill this gap in our understanding of the S_N2 reaction, we have investigated in some detail the energetics of frontside attack for a chemically more realistic system, $CH_3F + F^-$.

2. Calculations

The SCF wave functions used in the present work were calculated using the standard GAUSSIAN 70 program package [18] with the STO-3G and 4-31G basis sets [19, 20]. Computations were performed on the CDC Cyber 76 at Bologna (single precision arithmetic, 60-bit word) and on the IBM 360/91 at Princeton (double precision, 32-bit word).

A preliminary survey of the energy hypersurface of $CH_3F + F^-$ indicated that the STO-3G basis set was unsuitable for our purposes. As shown in the Appendix, and in contrast with better *ab initio* calculations [8] which predict the existence of a transition state for the S_N2 reaction with backside attack, calculations with the STO-3G basis set predict a stable intermediate. This suggests that estimates of geometries and energy differences obtained at the minimal basis set level can be grossly misleading. The 4-31G basis set, on the other hand, is capable of reproducing a (local) transition state (see below).

The geometry optimizations and energy calculations reported in the body of this paper were performed with the 4-31G basis set. It should be noted that this basis set is of double zeta quality in the valence region but does *not* contain angular polarization functions (i.e., *p* orbitals on H, *d* orbitals on C and F). The 4-31G basis set for fluorine is known to be poorer in quality than the carbon basis set [20]. Furthermore, it should be pointed out that anionic systems are notoriously difficult to represent accurately with small or moderate size basis sets [21]. Despite these known shortcomings, the 4-31G basis set was used in the present work. Since the location of intermediates and transition states requires an extensive search of geometries, computations with a larger, more accurate basis set were beyond our reach for economic reasons.

Some preliminary geometry optimization was performed with the built-in facilities of GAUSSIAN 70. Convergence to the final geometries was achieved with the force method [22, 23]. In this technique, the forces on the atoms in a molecule are calculated analytically (a process roughly as expensive as the calculation of the electronic energy of the molecule). Then these forces, along with force constants obtained either empirically or *ab initio* [23, 24], are used to locate the minima and transition states. The net result is a method of optimizing geometry that is several times faster than the conventional methods based only on the energy.

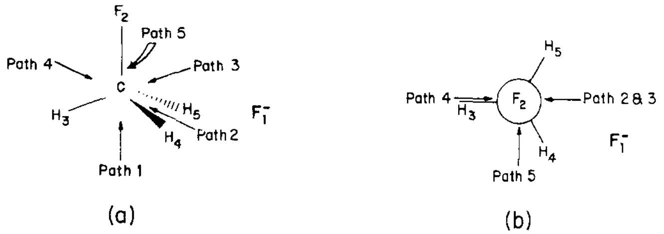
The magnitudes of the residual forces on the atoms in a molecule at its "optimized" geometry are measures of the accuracy of this optimization. For this reason, the "root mean square" (RMS) gradient[3] is also reported, in addition to the energy and optimized geometry. An RMS gradient of 0.005 mdyn or less is considered to be satisfactory. For a stable molecule at this level of convergence on the forces, it can be estimated that the energy would change by less than 0.2 kcal/mol, bond lengths by less than 0.002 Å and bond angles by less than 0.5° (based on forces and force constants calculated for CH_3F [25]). Estimates for transition states are more difficult to obtain, and because of their greater flexibility, a slightly lower degree of accuracy in the geometrical parameters can be expected for the same convergence on the forces.

3. Discussion

The attack of fluoride ion on methyl fluoride can be imagined to occur by way of five distinct paths, each characterized by a particular symmetry of the approach and the transition state. These paths can be defined in terms of edges, faces, and symmetry elements of the trigonal pyramid whose vertices are the four ligand atoms, as shown in Fig. 1. The fluoride ion can be allowed to approach:

1) the 3H face, along the C_3 axis in the usual backside attack[4],
2) a 2H edge, in a H-C-F plane,
3) a 2H, F face, in a H-C-F plane,
4) a H, F edge, in a H-C-F plane, and
5) in a plane which contains the C-F bond axis and which is perpendicular to the H-C-F plane.

Direct attacks on H or F have been excluded, as these would not lead to an S_N2 reaction. The relevant energies and geometries are collected in Table 1. The individual paths of approach are discussed in detail below.



(a) (b)

Fig. 1. Five possible paths of attack of fluoride ion on methyl fluoride: a) side view, b) top view

---

[3] RMS gradient $= \sqrt{\left(\sum_{i=1}^{n} g_i^2\right)\Big/ n}$, where g_i are the forces in the n internal coordinates.

[4] Path 1 has been included only for the purpose of calibration. For this particular mode of approach, there is no shortage of high quality calculations [2-14].

Table 1. Stable structures and transition states on the hypersurface for the S_N2 reaction $CH_3F + F^-$

	Structure						
	I	II	III	IV	V	VI	VII
Geometry[a]							
r_{CF_1}	∞	2.444	1.828	1.697	2.735	1.871	1.803
r_{CF_2}	1.412	1.462	1.828	1.373	1.446	1.750	1.803
r_{CH_3}	1.076	1.068	1.059	1.861	1.103	1.080	1.070
$r_{CH_4} = r_{CH_5}$	1.076	1.068	1.059	1.053	1.082	1.077	1.083
$\angle F_1CF_2$	180.0	180.0	180.0	94.9	233.8	278.7	81.9[c]
$\angle F_2CH_3$	108.3	108.3	90.0	92.9	112.8	152.8	98.2 (= $\angle F_1CH_3$)[c]
$\angle F_2CH_4$	108.3	108.3	90.0	117.5	106.2	86.0	110.7 (= $\angle F_1CH_5$)[c]
$\angle F_2CH_5$	108.3	108.3	90.0	117.5	106.2	86.0	77.0 (= $\angle F_1CH_4$)[c]
$\angle H_3CF_2H_4$,[b] $\angle H_3CF_2H_5$	±120.0	±120.0	±120.0	±82.2	±121.7	±124.0	
RMS gradient[d] (mdyn)	0.0013	0.0031	0.0012	0.0046	0.0011	0.0019	0.0049
Total Energy (Hartree)	−238.1064 −238.1255[e]	−238.1482	−238.1296	−238.0310	−238.1481	−238.0379	−238.0397
Energy relative to III (kcal/mol)	14.6 2.6[e]	−11.7	0.0	61.9	−11.6	57.6	56.4

[a] Bond lengths in Å, bond angles in degrees.

[b] Dihedral angles about the CF_2 axis; $\angle F_1CF_2H_3 = 180°$.

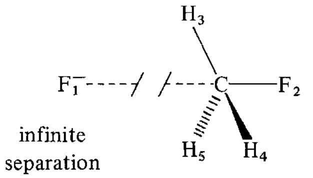
[c] For VII only; dihedral angles not used for the internal coordinate of VII.

[d] "Root Mean Square" gradient using the internal coordinates which specify the geometry; angles scaled by a unit bond length.

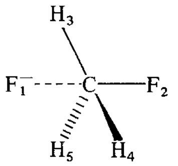
[e] Calculated for I using the counterpoise method.

3.1. Path 1

As the fluoride ion approaches the 3H face of methyl fluoride (I) the total energy decreases until an intermediate C_{3v} cluster (II) is reached at $r_{CF_1'} = 2.44$ Å. The C-F$_2$ bond lengthens by a small amount and the C-H bonds shorten slightly. A similar minimum has been found by Dedieu and Veillard [7, 8], although the actual geometrical parameters vary with the basis set employed.



I



II

In the C_{3v} cluster, the fluoride ion is relatively loosely bound. As shown in Fig. 2, the energy surface for the motion within the cone for backside approach is relatively flat, with the energy varying by only a few kcal/mol. More extensive calculations in this region of the surface (see path 4) suggest that an ion-molecule cluster with fluoride ion bound to a single hydrogen (i.e., vertex coordination) as opposed to three hydrogens (face coordination) may be just as stable.

Recently, it has become possible to observe S$_N$2 reactions in the gas phase [26–30]. Of particular interest in this connection is the observation, in ion cyclotron resonance [31] and mass spectrometric [30] experiments, that Cl$^-$, Br$^-$and I$^-$ form stable complexes with molecules such as CH$_3$X, X=F, Cl, Br, I. Results from triple resonance experiments [31] on the Cl$^-$-CH$_3$Cl system require the chlorines in the complex to be non-equivalent. This indicates that such ion-molecule clusters cannot represent "tran-

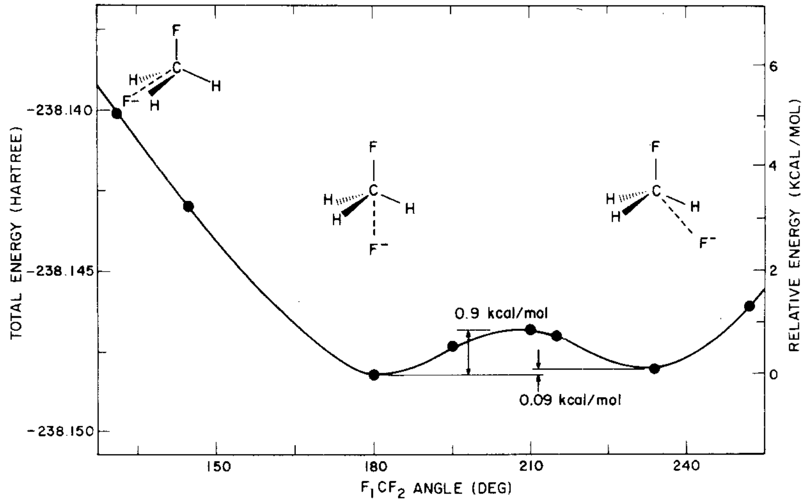
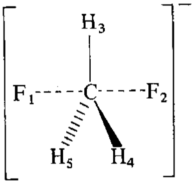


Fig. 2. Dependence of the energy on the F$_1$-C-F$_2$ angle in the ion-molecule cluster

sition states" for S_N2 reactions. Furthermore, isotopic labelling [32] and X-ray structural studies [33], as well as *ab initio* calculations [34], on formally analogous CX_5^- ions have shown that these molecules are not pentahalo-carbonato (IV) anions, i.e., species in which a pentacoordinate carbon is bonded to five halogen ligands. Instead, a halogen ion is loosely bound to one of the halogen atoms in CX_4 (vertex coordination). Our calculations are qualitatively in agreement with these findings.

In the light of this analysis, there is now reason to doubt the significance of recent attempts [30] to equate the properties of ion-molecule clusters observed in the gas phase with the properties of the transition state of the corresponding S_N2 reaction rather than with pre-transition state ion-molecule clusters. By the same token, statements [30] about solvation effects on the S_N2 reaction which are based on this premise would also seem to be unfounded. Instead, more direct measurements [26-29] should be used to deduce properties of the S_N2 reaction in the gas phase.

As the fluoride ion is brought closer to the central carbon atom, the energy increases until the D_{3h} transition state (III) is reached at $r_{CF} = 1.83$ Å. It is apparent from Table 1 that the C-H bonds in III are considerably shorter than in methyl fluoride.



III

The geometrical parameters and trends for I-III compare favorably with the results obtained by Dedieu and Veillard with larger basis sets [8]. However, if the energy of the transition state relative to the isolated reagents is compared to the corresponding results of Dedieu and Veillard, a large discrepancy is found. In the present work, the D_{3h} transition state is 14.6 kcal/mol more stable than the reagents, whereas Dedieu and Veillard found only 0.88 kcal/mol with a very large *sp* basis set [7]. The difference can be traced to the relatively poor description of the fluoride ion in the present work. When the energy of the reagents is recalculated by the counterpoise method[5], the D_{3h} transition state is only 2.6 kcal/mol more stable than the reagents, in reasonably good agreement with the results of Dedieu and Veillard [7].

Inclusion of angular polarization functions in the basis set raises the energy of the transition state relative to the reagents or the ion-molecule cluster II by ~8 kcal/mol

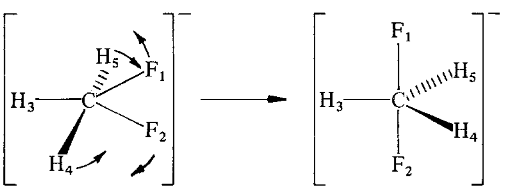
---

[5] The "functional counterpoise" method [35] is a technique for improving the quality of small energy differences by balancing the errors made in the individual energy computations. The fluoride ion was placed 2.5 Å from the central carbon of methyl fluoride (CH_3F at its optimum geometry in I) along path 1 and the energy was recalculated in the presence of the basis functions (but not the electrons or nuclei) of methyl fluoride. In this manner, the isolated fluoride ion is described with approximately the same accuracy as the F^- fragment in II or III. A definite improvement in the energy is obtained (cf. Table 1). When methyl fluoride is recalculated in the same manner (i.e., in the presence of the F basis functions), there is little improvement in the energy.

[8, 10, 12]. A similar effect should be anticipated for the fluoride ion attacking along other paths; thus, the relative energy of two transition states should be influenced to a lesser degree by polarization functions than the relative energy of a transition state and the reagents. Although the role of electron correlation in the course of the S_N2 reaction is uncertain [9, 13, 14], its effects should also be cancelled, for the most part, when energy differences between two transition states are taken. The actual effects of polarization functions and electron correlation cannot be tested within the limits of the present investigation and must await more extensive calculations at a later time. Keeping these *caveats* in mind, we may proceed to examine frontside attack of fluoride ion on methyl fluoride.

3.2. Path 2

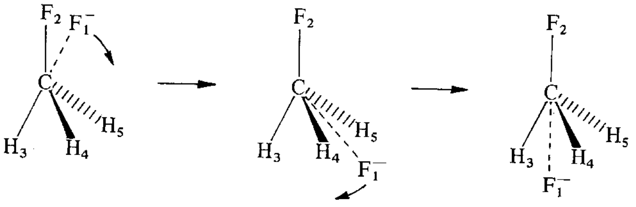
If successful, an attack along path 2 should lead to a C_{2v} trigonal bipyramidal transition state, with the two fluorine atoms equatorial. This structure is not stable and optimizes directly to the D_{3h} transition state, III. Hence there is no transition state of C_{2v} symmetry.



III

3.3. Path 3

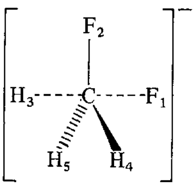
At C-F_1 distances of ~2.5 Å in the approach of fluoride ion to the 2H,F face of methyl fluoride, one might expect to find an ion-molecule cluster similar to II. Instead, geometry optimization leads directly to II, indicating that no stable cluster exists for attack along path 3 (coordination with the 2H,F face) or path 2 (coordination with the 2H edge).



II

Further attack on the 2H,F face should lead to a C_s transition state. Since there are no symmetry operations relating the two fluorine bonds, as was the case in paths 1 and 2, location of this transition state becomes problematic. The simplest approach is to fix the bond length of the incoming fluoride ion and to optimize all of the remaining parameters. Repetition of this procedure at decreasing values of the fixed bond length should, in principle, lead to the transition state.

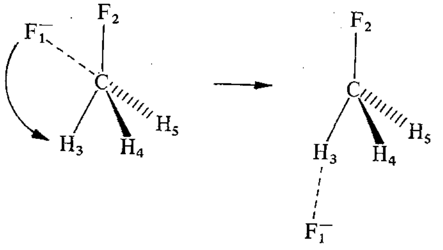
When this procedure is applied to the attack of F^- along path 3, the other C-F bond does not lengthen. Instead, the C-H bond opposite the attacking F^- extends until transition state IV is reached. Structure IV corresponds to the S_N2 displacement of hydride ion by fluoride via normal backside attack, an unwanted side reaction from the viewpoint of the present investigation. The reaction is very endothermic and, as expected, the transition state lies closer to the products than the reagents. The new $C\text{-}F_1$ bond is considerably shorter than in III, and the $C\text{-}H_3$ bond is longer than in the D_{3h} transition state of CH_5^- [8]. The shortening of the remaining bonds is more pronounced than in III.



IV

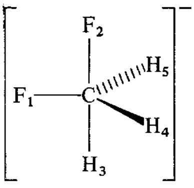
3.4. Path 4

A search for a stable ion-molecule cluster along path 4 leads to the cluster V. As indicated in Fig. 2, V is 0.09 kcal/mol less stable than II and separated from II by a barrier of *ca.* 0.8 kcal/mol. Since this energy difference is so small, it is not possible to state with certainty which of the two clusters is the more stable.



V

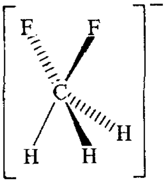
At closer approaches, attack of the fluoride ion along the H,F edge is unstable with respect to path 3. However, this mode of approach allows us to reach a different C_s transition state, which could have also been reached via path 3. Structure VI, obtained in this manner, leads to the S_N2 displacement of fluoride with retention of configuration. It is interesting to note that the equatorial $C\text{-}F_1$ bond is longer than the apical $C\text{-}F_2$ bond (cf. Table 1). No shortening of the non-participating C-H bonds is observed. A rationalization of this phenomenon is provided in the next section.



VI

3.5. Path 5

The transition state (VII), reached by letting the fluoride ion approach along a path in a plane perpendicular to a H-C-F plane, also leads to displacement with retention. Since VII is lower in energy than VI, structure VII is the true transition state, while VI is merely a local maximum in 2 of the 12 degrees of freedom. In an idealized turnstile rotation [36], structure VII can be derived from VI by a 30° torsion of the 2F group about an axis through the CH_3 group, followed by a geometry relaxation. Barriers in such six-fold rotors are typically very small [37]; this accounts for the small energy difference between VI and VII (cf. Table 1).



VII

Both VI and VII are lower in energy than IV; thus fluoride displacement with retention is energetically favored over hydride displacement with inversion. However, it should be borne in mind that other reactions, not directly considered here, can also occur with roughly the same energy requirements. For example, proton abstraction by fluoride ion results in hydrogen fluoride plus fluoromethyl carbanion, energy relative to III = ca. 60 kcal/mol (crude calculation with 4-31G basis set and no geometry optimization).

Transition state VII is remarkably similar to the one proposed by Stohrer [38] for an S_N2 reaction with retention. The present calculations, however, suggest that the transition state should be visualized as a two-fold rotor containing the nucleophile and the leaving group, rather than a three-fold rotor as suggested by Stohrer. A PMO analysis based on the present calculations [39] might be useful for qualitative discussions of stabilization and substituent effects.

4. Conclusion

In the previous sections, the principal features of the energy hypersurface describing the S_N2 reaction of fluoride ion and methyl fluoride have been located. Structures and relative energies of transition states corresponding to both frontside and backside attack have been discussed. Backside attack is unequivocally favored; frontside attack has been found energetically less favorable by ~ 56 kcal/mol. It is unlikely that these qualitative features of the energy hypersurface would be affected by an increase in the basis set size. In addition to transition states, two possible F^{-}-CH_3F clusters have been found. Since the energy difference between these structures is very small, verification of these findings with larger basis set calculations would appear to be worthwhile.

Acknowledgements. We thank the Italian CNR and the National Science Foundation (MPS74-18161) for support of this work, and Professor J. I. Brauman and Dr. W. N. Olmstead for helpful comments. One of us (H.B.S.) wishes to thank the National Research Council of Canada for a NATO Postdoctorate Fellowship.

Appendix

A preliminary survey of the path for the S_N2 reaction of fluoride ion with methyl fluoride with inversion is shown in Fig. 3. All points represent optimized geometries at the given, fixed C-F_1 distances using both the STO-3G and the 4-31G basis sets. These curves can be compared with the energy profiles published by Dedieu and Veillard [8] for calculation with higher quality basis sets. The 4-31G basis set correctly repro-

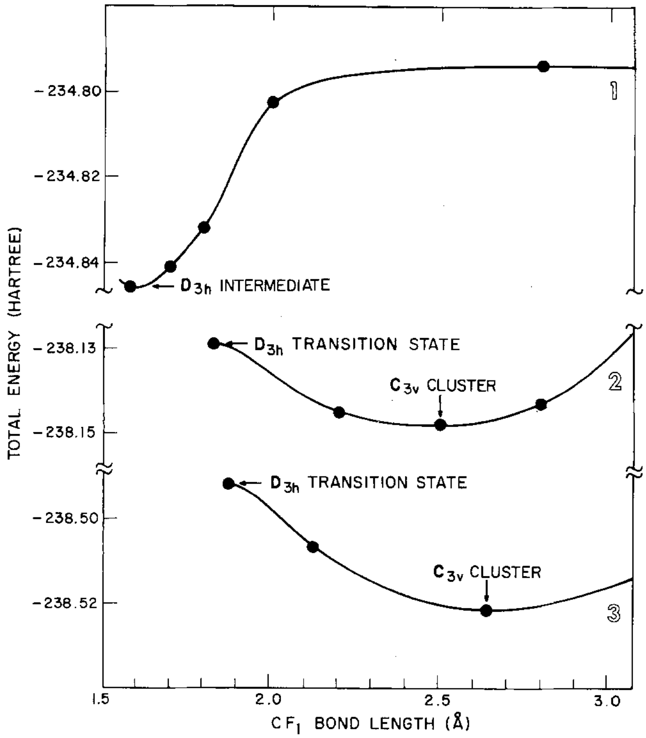


Fig. 3. Basis set dependence of the energy profile for backside attack of fluoride ion on methyl fluoride (path 1). Curve 1 was computed with the STO-3G basis set, curve 2 with the 4-31G basis set, and curve 3 by Dedieu and Veillard [8] with a large *spd* basis set

duces a local C_{3v} minimum and a D_{3h} transition state; the STO-3G basis set fails, producing instead a D_{3h} intermediate. A similar flaw found in certain semi-empirical calculations [16, 40] is probably due to the minimal basis set approximation rather than to the semi-empirical evaluation of the integrals.

This can be considered as an example for the following rule:

If the energy hypersurfaces at minimal and extended basis set levels are qualitatively the same, angular polarization functions will be relatively unimportant. Conversely, if the hypersurfaces are qualitatively different, polarization functions will be important.

This rule can be partially rationalized by the fact that radial and angular polarizations are not strictly separable for polyatomic systems.

References

1. Ingold, C. K.: Structure and mechanism in organic chemistry, Second Ed., Chapter 7. Ithaca, N.Y.: Cornell University Press 1969
2. Bader, R. F. W., Gangi, R. A.: In: Theoretical chemistry, Vol. 2, p. 1. The Chemical Society, A Specialists Periodical Report. London: Burlington House 1975
3. van der Lugt, W. Th. A. M., Ros, P.: Chem. Phys. Letters **4**, 389 (1969)
4. Mulder, J. J. C., Wright, J. S.: Chem. Phys. Letters **5**, 445 (1970)
5. Ritchie, C. D., Chappell, G. A.: J. Am. Chem. Soc. 92, 1819 (1970)
6. Berthier, G., David, D.-J., Veillard, A.: Theoret. Chim. Acta (Berl.) **14**, 329 (1969)
7. Dedieu, A., Veillard, A.: Chem. Phys. Letters 5, 328 (1970)
8. Dedieu, A., Veillard, A.: J. Am. Chem. Soc. 94, 6730 (1972)
9. Dedieu, A., Veillard, A., Roos, B.: In: Chemical and biochemical reactivity, p. 371. The Jerusalem Symposium on Quantum Chemistry and Biochemistry. Boston: D. Reidel 1974
10. Duke, A. J., Bader, R. F. W.: Chem. Phys. Letters **10**, 631 (1971)
11. Bader, R. F. W., Duke, A. J., Messer, R. R.: J. Am. Chem. Soc. **95**, 7715 (1973)
12. Baybutt, P.: Mol. Phys. **29**, 389 (1975)
13. Keil, F., Ahlrichs, R.: J. Am. Chem. Soc. 98, 4787 (1976)
14. Dyczmons, V., Kutzelnigg, W.: Theoret. Chim. Acta (Berl.) **33**, 239 (1974)
15. Fukui, K., Fujimoto, H., Yamabe, S.: J. Phys. Chem. 76, 232 (1972); Fujimoto, H., Yamabe, S., Fukui, K.: Tetrahedron Letters 439 (1971); Tetrahedron Letters 443 (1971)
16. Gillespie, P., Ugi, I.: Angew. Chem. **83**, 493 (1971)
17. Schmid, G. H., Hallman, G. M.: J. Mol. Struct. **18**, 489 (1973)
18. Hehre, W. J., Lathan, W. A., Ditchfield, R., Newton, M. D., Pople, J. A.: Gaussian 70 Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana
19. Hehre, W. J., Stewart, R. F., Pople, J. A.: J. Chem. Phys. **51**, 2657 (1969)
20. Ditchfield, R., Hehre, W. J., Pople, J. A.: J. Chem. Phys. **54**, 724 (1971)
21. Ahlrichs, R.: Chem. Phys. Letters **34**, 570 (1975)
22. Pulay, P.: Mol. Phys. 17, 197 (1969)
23. Schlegel, H. B.: Ph.D. Thesis, Queen's University (1975)
24. Pulay, P., Meyer, W.: Mol. Phys. 27, 473 (1974) and earlier work
25. Schlegel, H. B., Wolfe, S., Bernardi, F.: To be published
26. Bohme, D. K., Mackay, G. I., Payzant, J. D.: J. Am. Chem. Soc. **96**, 4027 (1974)
27. Payzant, J. D., Tanaka, K., Betowski, L. D., Bohme, D. K.: J. Am. Chem. Soc. **98**, 894 (1976)
28. Lieder, C. A., Brauman, J. I.: J. Am. Chem. Soc. **96**, 4028 (1974)
29. Brauman, J. I., Olmstead, W. N., Lieder, C. A.: J. Am. Chem. Soc. **96**, 4030 (1974)
30. Dougherty, R. C., Dalton, J., Roberts, J. D.: Org. Mass Spectrom. **8**, 77 (1974); Dougherty, R. C., Roberts, J. D.: Org. Mass Spectrom. 8, 81 (1974); Dougherty, R. C.: Org. Mass Spectrom. 8, 85 (1974)

31. Riveros, J. M., Breda, A. C., Blair, L. K.: J. Am. Chem. Soc. **95**, 4066 (1973)
32. Effenberger, F., Podszun, W., Schoeller, W. W., Seufert, W. G., Stohrer, W.-D.: Chem. Ber. **109**, 306 (1976)
33. Lindner, H. J., Kitsche-von Gross, B.: Chem. Ber. **109**, 314 (1976)
34. Wang, S.-J.: Z. Naturforsch. **28a**, 1832 (1973)
35. Boys, S. F., Bernardi, F.: Mol. Phys. **19**, 553 (1970)
36. Ugi, I., Marquarding, D., Klusacek, H., Gillespie, P., Ramirez, F.: Acc. Chem. Res. **4**, 288 (1971)
37. Tel, L. M., Wolfe, S., Csizmadia, I. G.: Intern. J. Quantum Chem. **7**, 475 (1973)
38. Stohrer, W.-D., Schmieder, K. R.: Chem. Ber. **109**, 285 (1976)
39. Bernardi, F., *et al.*: in progress
40. Woolley, A. M., Child, M. S.: Mol. Phys. **19**, 625 (1970); Allinger, N. L., Tai, J. C., Wu, F. T.: J. Am. Chem. Soc. **92**, 579 (1970); Cremaschi, P., Gamba, A., Simonetta, M.: Theoret. Chim. Acta (Berl.) **25**, 237 (1972)
41. Keil, F., Kutzelnigg, W.: J. Am. Chem. Soc. **97**, 3623 (1975)

Received June 21, 1976/August 25, 1976