

Usefulness of one electron properties in the study of the nitromethane-to-methyl nitrite rearrangement

S. Roszak,* A. H. Lowrey,† W. A. Sokalski* and Joyce J. Kaufman‡

*Institute of Physical and Theoretical Chemistry (I-4), Wrocław, Poland

†Laboratory for the Structure of Matter, Naval Research Laboratory, Washington DC

‡Department of Chemistry, The Johns Hopkins University, Baltimore, MD, USA

Large-scale multiple reference configuration interaction calculations for a unimolecular rearrangement reaction of nitromethane to methyl nitrite are presented. The complicated structure of potential energy curves is explained in terms of interactions between ground and excited states. An explanation for an extremely long C—N and C—O bond distances in the transition state is also given. The study of corresponding dipole moments and electrostatic molecular potentials enhances the overall understanding of the reaction.

Keywords: electrostatic potential, cumulative atomic multiple moments (CAMP), multiple reference double-excitation configuration interaction method (MRD-CI), nitromethane–methyl nitrite rearrangement, electronic excited states

INTRODUCTION

The unimolecular rearrangement of nitromethane to methyl nitrite is a dissociation process which competes with the simple C—N bond rupture.¹ This reaction may serve as a prototype for many known nitro–nitrite rearrangement processes.^{2–4} The theoretical study of rearrangement reactions has been performed for the case of nitromethane^{5,6} and nitramine.⁷ A common feature of transition states in these reactions is extremely long bonds which are directly involved in the unimolecular rearrangement, and relatively little change in other structural parameters. The multireference configuration interaction (MRD-CI) studies of C—N and N—N bond scission^{8,9} indicate that the ground state potential surfaces interact strongly with corresponding excited states, and that dissociation processes involve

avoided crossings, which allows the reaction products to become radicals. The reaction can be seen as a superposition of two simple decomposition reactions in the direction toward the transition state. The proper understanding of the rearrangement reaction thus requires a study of the properties of the electronic ground state, together with the corresponding excited states. The avoided crossing is not apparent at first glance because the interaction between the diabatic curves corresponding to the ground and excited states is very strong and leads to an unusually large separation between the curves.¹⁰ These interactions may be confirmed by looking at the wavefunction or related properties. In this work, we present the results of large-scale MRD-CI calculations for the singlet ground state and the corresponding lowest-lying singlet excited state. The composition of the wavefunction and one electron properties, dipole moment, and molecular electrostatic potentials are presented together with potential energy curves. The studies of these properties enhances the overall understanding of this reaction.

METHODOLOGY

MC-SCF geometry optimization

The full Multiconfiguration Self Consistent Field (MC-SCF) optimization of nitromethane and methyl nitrite structures for different C—N and C—O bond distances was performed for the ground state wavefunctions. The optimization was performed using GAMESS program package.¹¹ The MC-SCF active space has been composed from the three highest occupied and three lowest virtual molecular orbitals. Such a choice guarantees that the most active molecular orbitals, corresponding to $\sigma(\text{C—N})$ in the nitromethane case and $\sigma(\text{C—O})$ in the methyl nitrite case, will be included in the active space.⁸

MRD-CI calculations

The configuration interaction treatment employed was the standard Buenker and Peyerimhoff multiple reference dou-

Color Plates for the article are on page 197.

Received 2 September 1993; revised 1 February 1994; accepted 17 February 1994

Address reprint requests to Dr. Lowrey at the Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375, USA.

ble-excitation configuration interaction (MRD-CI) method with configuration selection and use of perturbative corrections. The computations were carried out employing Table CI algorithm.¹² The eigenvalues, together with the summed perturbative energy lowerings of the nonselected configurations in the total MRD-CI space, were then employed^{13,14} to determine an extrapolated zero-threshold value, ($E_{\text{EX,MRD-CI}}$). The energy corresponding to the full CI treatment was estimated by the relation

$$E_{\text{FCI}} = E_{\text{EX,MRD-CI}} + (E_{\text{EX,MRD-CI}} - E_{\text{ref}}) \left(1 - \sum_i^{\text{ref}} c_i^2 \right) \quad (1)$$

which is a multireference generalization¹⁵ of the correction formula suggested by Langhoff and Davidson,¹⁶ where E_{ref} is the reference secular equation energy. A recent paper by Buenker and coworkers¹⁷ demonstrates that MRD-CI calculations with the multireference Davidson correction compare very closely with full CI calculations.

The MRD-CI calculations were performed using integral and SCF routines of the ATMOL 3 program,¹⁸ and the transformation and CI routines of the MRD-CI program.¹⁹

Molecular Electrostatic Potentials

The general expression for a molecular electrostatic potential (MEP) has the form:

$$V(\vec{r}) = \sum_{\alpha}^{\text{nuclei}} Z_{\alpha}/(|\vec{r}_{\alpha} - \vec{r}|) - \int d\vec{r}_1 \rho(\vec{r}_1)/|\vec{r}_1 - \vec{r}| \quad (2)$$

The potential $V(\mathbf{r})$ can also be expressed by employing multipoles from any infinite multicenter multipole expansion.²⁰

Among several multicenter multipole expansions^{21–25} which yield practically equivalent results,²⁴ one of the simplest can be obtained^{25–27} from the expression

$$M_a^{klm} = Z_a u_a^k v_a^l w_a^m - \sum_{I \in a} \sum_J^{AO} P_{IJ} \langle I | u^k v^l w^m | J \rangle - \sum_{k' \geq 0}^k \sum_{l' \geq 0}^l \sum_{m' \geq 0}^m \begin{pmatrix} k \\ k' \end{pmatrix} \begin{pmatrix} l \\ l' \end{pmatrix} \begin{pmatrix} m \\ m' \end{pmatrix} u_a^{k-k'} v_a^{l-l'} w_a^{m-m'} M_a^{k'l'm'} \quad (3)$$

where Z_a denotes the nuclear charge of the a th atom, $\langle I | u^k v^l w^m | J \rangle$ denotes the one electron multipole moment integral, and P_{IJ} denotes the first-order reduced density matrix element ($u, v, w = x, y, z$). The first two terms in Equation (3) are equivalent to the atomic charge definition within Mulliken population analysis, (M_a^{000}).²⁹ The higher order cumulative atomic multipole moments (CAMM), M_a^{klm} , obtained from the recursive formula (3) represent details of the molecular charge distribution not described by lower moments.^{25–28} In this work, the values of MEP on the molecular surface points have been calculated including atomic charges, dipoles and quadrupoles.²⁰ The matrix elements P_{IJ} were calculated within the multiple reference single- and double-excitation configuration interaction method (MRD-CI).

TECHNICAL DETAILS OF THE THEORETICAL TREATMENT

In the present work an atomic orbital (AO) basis proposed by Huzinaga,³⁰ with the contraction scheme of Dunning,³¹ was employed. The basis consists of nine s and five p primitive gaussians in a $[4s2p]$ contraction for carbon, nitrogen, and oxygen atoms, and four s functions contracted to $[2s]$ for hydrogen. In addition, a set of Cartesian d polarization functions was placed on heavy atoms, and a set of p functions was placed at each hydrogen atom, with exponents taken from Dunning and Hay.³² This choice leads to a total of 79 atomic orbitals.

A core of four molecular orbitals corresponding to the 1s shells of heavy atoms was kept doubly occupied in all MRD-CI calculations, and the 10 virtual molecular orbitals (MOs) with highest orbital energies were discarded at the transformation stage. The remaining 60 MOs were used for the generation of single and double excitations relative to a given electronic state. Single and double excitations from the most important 10 reference configurations were considered, about 2,000,000 symmetry adapted functions (SAFs) in all. All configurations below the selection threshold of 40 μH were explicitly included, approximately 9000 SAFs. The estimate of the full CI energy was done by extrapolating and adding the Davidson correction, as described in the previous section.

Molecular electrostatic potentials are displayed on atomic van der Waals surfaces using the program Mol 17 (see Color Plate 1).²⁰ The colors represent values of the electrostatic potential, going from the most negative to the most positive in the following order: yellow, red, pink, white, light blue, bright blue, and cyan. The upper and lower limits of the potential were chosen to be ± 50.0 kcal/mol; all potential values greater than $+50.0$ were made cyan, and all values less than -50.0 were made yellow.

RESULTS OF MC-SCF GEOMETRY OPTIMIZATION

The study of the nitromethane–methyl nitrite rearrangement pathway requires structure optimization for different values of the reaction coordinate. Since only the equilibrium structures and transition state are available from the literature, we have optimized again the equilibrium structures and structures for additional points on the reaction pathway. The results for equilibrium structures (Figure 1, Tables 1 and 2) are in reasonable agreement with experimental data, as well as with previous theoretical results. The energy difference between equilibrium structures is 5.37 kcal/mol (without the zero point vibrational energy correction), and is in reasonable agreement with the experimental value of 2.07 kcal/mol.³³ The structure of the transition state has been adopted from McKee.⁶

MRD-CI POTENTIAL ENERGY CURVES

The potential surfaces for the nitromethane-to-methyl nitrite rearrangement have a complicated structure in both the ground and excited states. The nature of these curves cannot be understood without the detailed study of their wavefunction. The ground state surface is shifted from the purely diabatic structure due to strong interactions with the corre-

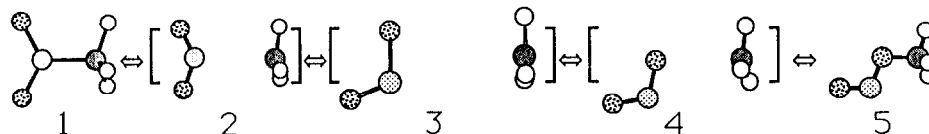


Figure 1. Structures for nitromethane, the transition state, and methyl nitrite along the rearrangement pathway.

Table 1. Structural parameters for nitromethane

Parameter	MCSCF	MCSCF ⁶	Experiment ³⁷
C—N (Å)	1.482	1.474	1.481
N—O (Å)	1.228	1.205	1.215
C—H (Å)	1.098	1.081	1.098
<NCH (°)	108.5		107.3
<ONO (°)	125.4		123.3

Table 2. Structural parameters for methyl nitrite

Parameter	MCSCF	MCSCF ⁶	Experiment ³⁸
C—O (Å)	1.410	1.417	1.435
N—O (Å)	1.347	1.339	1.451
N=O (Å)	1.206	1.179	1.170
C—H (Å)	1.106	1.081	1.099
<OCH (°)	111.2	113.1	111.0
<CON (°)	110.5		107.8
<ONO (°)	110.3		110.2

sponding excited state. The calculated excitation energy for nitromethane of 4.537 eV agrees with the experimentally known lowest singlet-singlet transition of 4.59 eV.³⁴ The potential energy curves are presented on Figure 2, and main components of the wavefunction are presented in Table 3. Based on these data, three different geometrical arrangements may be selected: nitromethane, the transition state, and methyl nitrite. The decomposition of nitromethane appears as an increase in the coefficient corresponding to the $\sigma(\text{C—N}) \rightarrow \sigma^*(\text{C—N})$ transition of the ground state wavefunction and an increase of the SCF configuration in the excited state wavefunction. The small change in the balance between configurations building the total wavefunction is sufficient to swap the character of the ground and excited state. The existence of the avoided crossing around the $R[\text{C—N}] = 2.2$ Å, barely seen from the wavefunction structure, is clearly demonstrated by MEP maps described later. The same behavior, but with a sudden change in coefficients, is found in the methyl nitrite decomposition toward the transition state. In this case, the obvious avoided crossing is visible in the wavefunction structure between $R[\text{C—O}] = 2.2$ Å and $R[\text{C—O}] = 2.9$ Å. The wavefunction of the transition state has a completely different structure than its substrate or product partners, and wavefunctions in both electronic states are a mixture of SCF and HOMO/LUMO configurations. The nitromethane side of the path closely resembles the nitromethane decomposition to NO_2 and CH_3 fragments.⁸ The methyl nitrite has not been

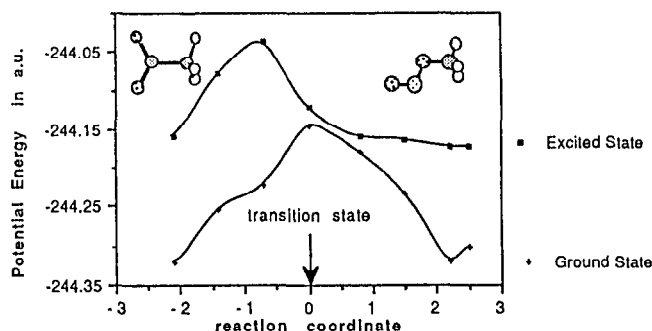


Figure 2. MRD-CI potential energy curves for the singlet ground and excited states for the nitromethane-to-methyl nitrite rearrangement reaction pathway.

studied in that detail, but is likely to proceed in a manner similar to the total decomposition.

The comparison of geometrical parameters (Figure 1) indicates that the decomposition of both partners proceeds toward the transition state as a simple C—N or C—O bond scission. At a point close to the transition state, the ONO group rotates from the $\text{CH}_3 \dots \text{NO}_2$ complex to the $\text{CH}_3 \dots \text{ONO}$ complex.

DIPOLE MOMENTS AND ELECTROSTATIC POTENTIAL SURFACES

The shape of the potential energy surfaces does not give a definitive explanation of properties for the rearrangement pathway. Dipole moments and molecular electrostatic potentials were studied to visualize the properties of the wavefunction and to help in the interpretation of the observed phenomena.

The dipole moment is a simple measure of the charge distribution in the system. For equilibrium structures it may be verified experimentally, reflecting the quality of the wavefunction calculations. The calculated ground state dipole moment for nitromethane (3.81D) agrees reasonably with available experimental values of 3.1–3.57D.³⁵ Much more detailed information on the charge distribution is carried by the electrostatic potential surfaces. An additional feature of these surfaces is the direct relation to the molecular reactivity indices.³⁶

The dipole moment values for representative points are presented in Table 4. Again, three different geometries can be recognized. The regions of nitromethane and methyl nitrite additionally have subregions characterized by the switch of dipole moment values. The avoided crossing around C—N bond = 2.2 Å, in the case of nitromethane, is clearly demonstrated by a sudden change in the dipole moment. Dissociated nitromethane has a very small dipole moment, while an excited state has a relatively large one.

Table 3. MRD-CI squares of coefficients (c^2) for important configurations for the ground state and excited singlet states for representative points of the nitromethane-to-methyl nitrite rearrangement reaction

Electronic configuration	Nitromethane R (C—N) 1.5 Å	Nitromethane R (C—N) 2.2 Å	Nitromethane R (C—N) 2.9 Å	Transition state R (C—N) 3.617 Å	Methyl nitrite R (C—O) 2.9 Å	Methyl nitrite R (C—O) 2.2 Å	Methyl nitrite R (C—O) 1.41 Å
Ground state							
SCF	0.882	0.883	0.695	0.188	0.033	0.853	0.887
HOMO/ LUMO	0.000	0.140	0.057	0.535	0.738	0.000	0.000
Excited state							
SCF	0.000	0.026	0.145	0.636	0.801	0.000	0.000
HOMO/ LUMO	0.847	0.780	0.577	0.209	0.036	0.803	0.813

Table 4. Dipole moments for the ground state and excited singlet states for representative points of the nitromethane-to-methyl nitrite rearrangement pathway (in Debye's)

Electronic configuration	Nitromethane R (C—N) 1.5 Å	Nitromethane R (C—N) 2.2 Å	Nitromethane R (C—N) 2.9 Å	Transition state R (C—N) 3.617 Å	Methyl nitrite R (C—O) 2.9 Å	Methyl nitrite R (C—O) 2.2 Å	Methyl nitrite R (C—O) 1.41 Å
Ground state	3.809	4.538	0.271	5.394	1.632	6.517	3.011
Excited state	3.464	3.859	11.781	7.068	8.667	3.137	6.538

This indicates that the molecule has already dissociated into two radicals in the ground state, and into charged species in the excited state. The methyl nitrite side has the same features, but they are not so sharply visible as in the nitromethane case. The transition state has a peculiar structure, where both states are very similar with respect to their electron density distributions. The interaction, which leads to two almost degenerate states, also causes the dipole moments to be similar. The high value of the dipole moment in both states is related to the asymmetric charge distribution in the NO_2 group and the long C—O and C—N bonds.

Electrostatic potential surfaces (representative points are presented in Color Plate 1) enhance the information coming from the dipole moment study. The ground state decomposition of nitromethane into two radicals with the ground state and into ionic species with the excited state is easily seen. This dissociation appears to be rapid, with the avoided crossing occurring somewhere before the C—N bond stretches to 2.2 Å. The occurrence of the avoided crossing is not evident from simple examination of the wavefunctions. It is also evident that the dissociation of methyl nitrite does not occur so rapidly. At $R[\text{C—O}] = 2.2$ Å, the ground state of methyl nitrite still exists as a pair of ions. The ionic decomposition path continues at $R[\text{C—O}] = 2.9$ Å but primarily in the excited state. Because of the less symmetric structure for methyl nitrite, the electronic distribution is more complicated, and this creates the less definitive appearance of the MEP maps. Potential surfaces are more diffuse, and the difference between the ground and excited states is not as striking. The transition state does not belong to either of the dissociation paths. The transition state has its specific struc-

ture with both the ground and excited states being very similar. The degeneracy at the transition state is manifested as similar MEP maps. The "radical" ground state is contaminated with the "ionic" excited state. This is demonstrated by the Mulliken population on the CH_3 radical, 0.25 electrons. The CH_3 population in the ionic excited state is only 0.40 electrons. This is visible in the similarity between the ground and excited MEP maps at the transition state. One view is that the dissociation paths of nitromethane and methyl nitrite are parallel and that the transition state is a saddle point between them. The ground state MEP for methyl nitrite at $R[\text{C—O}] = 2.9$ Å resembles the ground state MEP for the transition state. The MEP maps suggest that there is a continuity for the dissociation path in the ground state wavefunctions including the transition state. This continuity is not evident for the excited state wavefunctions, which suggests strong interactions with higher excited states. Studies of potential surfaces for higher excited states are needed to resolve the process of the reaction in the excited state.

DISCUSSION

The reaction pathway for the nitromethane–methyl nitrite rearrangement has a very complicated structure due to strong interactions between the ground and excited states. The pathway, to some extent being a superposition of two decomposition reactions, may be divided into five regions corresponding to nitromethane dissociation a) before and b) after avoided crossing, c) a transition state, and formation of methyl nitrite d) before, and e) after avoided crossing. The

rearrangement reaction requires that the fragments become radicals. In the case of radicals, electrostatic forces no longer determine the direction of interactions, and the complex may easily undergo rearrangement. This requirement leads to extremely long bonds $\{R[C-N] = 3.617 \text{ \AA}$ and $R[C-O] = 3.706 \text{ \AA}\}$ in the transition state.

The CI excitation coefficients affect the calculated properties; however, these relationships are not linear. The second factor is the structure of the molecular orbitals, which are different for each point on the reaction pathway. One electron properties which are computed from the wavefunction of the configuration interaction model are a nonlinear balance between CI coefficients and the structure of the molecular orbitals. The study of the nitromethane to methyl nitrite rearrangement shows the direct usefulness of the dipole moments and MEP in the interpretation of the reaction mechanism. The graphical representation of MEP maps is particularly useful because of its relationship to chemical intuition.

ACKNOWLEDGEMENTS

The authors thank Prof. R. J. Buenker, University of Wuppertal, Wuppertal, Germany, for his collaboration in adapting his MRD-CI program at The Johns Hopkins University, and V. R. Saunders, Daresbury Laboratory, UK, for his Atmol 3 and 5 program system and his collaboration in adapting this program at The Johns Hopkins University. The authors thank M. S. Gordon and M. W. Schmidt for sending us a FORTRAN copy of GAMESS.

This research was supported by ONR under Grant N00014-89-J-1613 and Contract N00014-80-C-003. The calculations were carried out on the CRAY YMP at the NSF San Diego Supercomputer Center. The authors thank the Center for the grant of computer time.

The graphics were created at the RCD Visualization Facility at the Naval Research Laboratory.

REFERENCES

- Wodke, A.M., Hints, E.J., and Lee, Y.T., *J. Phys. Chem.* 1990, **90**, 3549
- Gonzalez, A.C., Larson, C.W., McMillen, D.F., and Golden, D.M., *J. Phys. Chem.* 1985, **89**, 4809
- Tsang, W., Robaugh, D., and Mallard, W.G., *J. Phys. Chem.* 1986, **90**, 5968
- Stewart, P.H., Jeffries, J.B., Zellweger, J.M., McMillen, D.F., and Golden, D.M., *J. Phys. Chem.* 1989, **93**, 3557
- McKee, M.L., *J. Am. Chem. Soc.* 1986, **108**, 5784
- McKee, M.L., *J. Phys. Chem.* 1989, **93**, 7365
- Saxon, R.P. and Yoshimine, M., *J. Phys. Chem.* 1989, **93**, 3130
- Roszak, S. and Kaufman, J.J., *J. Chem. Phys.* 1991, **94**, 6030
- Roszak, S. and Kaufman, J.J., *Chem. Phys.* 1992, **160**, 1
- Kaldor, U., Roszak, S., Hariharan, P.C., and Kaufman, J.J., *J. Chem. Phys.* 1989, **90**, 6395
- Schmidt, M.W., Boatz, J.A., Baldridge, K.K., Koseki, S., Gordon, M.S., Elbert, S.T., and Lam, B., GAMESS program, *QCPE Bulletin*, 1990, **10**, 52
- Buenker, R.J. and Peyerimhoff, S.D., in *New Horizons of Quantum Chemistry* (P. O. Lowdin and B. Pullman, Eds.) Reidel, Dordrecht, 1983, p. 183; Buenker, R.J., Peyerimhoff, S.D., and Butcher, W., *Mol. Phys.* 1981, **35**, 771; Buenker, R.J., in *Proceedings of Workshop on Quantum Chemistry and Molecular Physics*, Wolongong, Australia, 1980; Buenker, R.J., in *Studies in Physical and Theoretical Chemistry*, Vol. 21, *Current Aspects of Quantum Chemistry* (R. Carbo, Ed.) Elsevier Scientific, Amsterdam, 1982, p. 17; Buenker, R.J. and Phillips, R.A., *J. Mol. Structure. (Theochem)*, 1985, **123**, 291
- Buenker, R.J. and Peyerimhoff, S.D., *Theor. Chim. Acta.* 1974, **35**, 33
- Buenker, R.J. and Peyerimhoff, S.D., *Theor. Chim. Acta.* 1975, **39**, 217
- Peyerimhoff, S.D. and Buenker, R.J., *Chem. Phys.* 1979, **42**, 167
- Davidson, E.R., in *The World of Quantum Chemistry* (R. Daudel and B. Pullman, Eds.) Reidel, Dordrecht, 1979, p. 17; Langhoff, S.R. and Davidson, E.R., *Int. J. Quant. Chem.* 1974, **8**, 61
- Knowles, D.B., Alvarez-Collado, J.R., Hirsh, G., and Buenker, R.J., *J. Chem. Phys.* 1990, **92**, 585
- Saunders, V.R. and Guest, M.F., ATMOL 3 Program System, Computational Science Group, SERC Daresbury Laboratory, Warrington, England; Saunders, V.R., Atmol 5 Program, 1990
- Buenker, R.J., MRD-CI Program System, Lehrstuhl Fur Theoretische Chemie, Gesamthochschule, University of Wuppertal, Wuppertal, Germany
- Sokalski, W.A. and Sneddon, S.F., *J. Mol. Graphics* 1991, **9**, 74
- Stone, A.J., *Chem. Phys. Lett.* 1981, **83**, 233
- Vigne-Maeder, F. and Claverie, P., *J. Chem. Phys.* 1988, **88**, 4934
- Mezei, M. and Campbell, E.S.C., *Theor. Chim. Acta.* 1977, **43**, 227
- Spackman, M., *J. Chem. Phys.* 1986, **85**, 6587
- Sokalski, W.A. and Poirier, R.A., *Chem. Phys. Lett.* 1983, **98**, 86
- Sokalski, W.A. and Sawaryn, A., *J. Chem. Phys.* 1987, **87**, 526
- Sawaryn, A. and Sokalski, W.A., *Comp. Phys. Comm.* 1989, **52**, 397
- Sokalski, W.A., Keegstra, P.B., Roszak, S., and Kaufman, J.J., *Int. J. Quant. Chem. Symp.* 1990, **24**, 51
- Mulliken, R.S., *J. Chem. Phys.* 1955, **23**, 1833
- Huzinaga, S., *J. Chem. Phys.* 1965, **42**, 1293
- Dunning, Jr., T.H., *J. Chem. Phys.* 1970, **53**, 2823
- Dunning, Jr., T.H. and Hay, P.J., in *Modern Theoretical Chemistry* (H.F. Schaefer III, Ed.) Plenum Press, New York, 1977, Vol. 3
- Cox, J.D. and Pilcher, G., *Thermochemistry of Organic and Organometallic Compounds*, Academic, London, 1970
- Nagakura, S., *Mol. Phys.* 1960, **3**, 152
- McClellan, A.L., *Tables of Experimental Dipole Moments*, Freeman, San Francisco, 1963
- Sadlej, J., *Semi-Empirical Methods of Quantum Chemistry*, Ellis Horwood Limited, Chichester, 1985
- Trevino, S.F., Prince, E., and Hubbard, C.R., *J. Chem. Phys.* 1980, **73**, 2996
- Turner, P.H., Corkil, M.J., and Cox, P.A., *J. Phys. Chem.* 1979, **83**, 1473