On the usefulness of generalised quantum chemical valence parameters in monitoring the course of a chemical reaction: A case study of the photochemical decomposition of HNO in excited states

D K MAITY, K K DAS[†] and S P BHATTACHARYYA[*]

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, India
[†] Present address: Department of Chemistry, Arizona State University, Tempe, Arizona 85287, USA

Abstract. A variant of the orthogonal gradient method of orbital optimization in the INDO-MCSCF framework has been used to study the photochemical decomposition of the HNO molecule into H + NO in the lowest $^{1,3}A''$ states. A complete geometry optimization has been carried out at all points of the reaction path which appears to be almost barrierless. The one-electron density matrix extracted from the optimized wavefunction at each point has been used to generate the relevant sets of quantum chemical valence parameters. A sharp transition is noted in the N–H bond order and hydrogen free valence index when plotted as functions of r_{NH}. This enables us to locate the transition region easily.

1. Introduction

HNO is an interesting molecule on many counts. From a purely chemists' point of view it is important because HNO is an intermediate in the NO-catalysed recombination of H atoms forming H_2 molecules. The heat of formation of HNO (in the reaction $H + NO \rightarrow HNO$) is known to be 48 kcal/mol. However, the N–H stretching frequency is significantly lower when compared to normal C–H stretching mode values. Photochemically, the interesting aspects concern the location of the lowest triplet ($^3A''$), chemiluminescence from the first excited singlet ($^1A''$) state, sudden disappearance of rotational structure of the 0–0 band in the emission spectrum etc.

Being a small molecule it has naturally been the target of a number of *ab initio* theoretical investigations at the SCF as well as SCF–CI levels. While *ab initio* SCF theoretical data (Wu *et al* 1975; Bruna and Marian 1979) predict the existence of a large activation barrier (~ 17 kcal/mol) in the photochemical decomposition of $HNO \rightarrow H + NO$ in the $^{1,3}A''$ states, inclusion of CI (without the optimization of geometry) reduces (Nomura 1980) the computed barrier in the $^1A''$ state sharply (~ 3 to 5 kcal/mol). It may be speculated that full geometry optimization at the CI level

---

* For correspondence

may reduce the computed barriers even further. The experimental scenario is equally puzzling. Kinetic data on the recombination of $H + NO \rightarrow HNO$ point to the existence of a zero or vanishingly small activation barrier (Clyne and Thrush 1960, 1961; Hartley and Thrush 1967). If one examines the relevant sections of the computed $^1A''$ potential energy surface one notes that the transition region is very broad (Nomura 1980) ranging over rather large N–H bond distances making it very difficult to locate the saddle point. It would probably be interesting to monitor some characteristic feature of the N–H bond itself along the reaction path which hopefully may show a sharp (at least sharper than energy) transition at the bond-breaking point. The quantities that immediately come to mind are the quantum chemical bond order of the bond that is being broken and the free valence index of the atom that is leaving.

2. The method

The variational trial function ($\tilde{\Psi}$) for the lowest A'' states are chosen in the following form:

$$\tilde{\Psi} = \frac{1}{\sqrt{2}} \{ |\phi_1 \bar{\phi}_1 \cdots \phi_i \bar{\phi}_j \cdots \phi_n \bar{\phi}_n| + (-1)^s |\phi_1 \bar{\phi}_1 \cdots \phi_j \bar{\phi}_i \cdots \phi_n \bar{\phi}_n| \},$$

where ϕ_i and ϕ_j are the relevant orbitals involved in the transition and $s = 0$ for the singlet and 1 for the triplet coupling of the spins. We have not included any more configurations in $\tilde{\Psi}$, for the simplest form chosen for $\tilde{\Psi}$ leads to the correct dissociation behaviour in the lowest A'' states. The variational problem therefore boils down to the solution of the MCSCF orbital equation only (cf. master equation of McWeeny 1968, McWeeny and Mukherjee 1970)

$$V = ST\lambda. \tag{1}$$

In (1) S is the matrix of the AO basis set of expansion (χ), T the matrix of the LCAO expansion coefficients of the MO (Φ) ($N \geqslant n$):

$$\Phi(|\phi_1\rangle, |\phi_2\rangle \cdots |\phi_n\rangle) = \chi(|\chi_1\rangle, |\chi_2\rangle \cdots |\chi_N\rangle) T(N \times n),$$

λ is the matrix of Lagrangian multipliers which must be Hermitian at the stationary point:

$$\lambda^\dagger = \lambda. \tag{2}$$

The MCSCF operator (V) is represented in a mixed AO–MO basis and is given by

$$V = hTP_1 + Z(P_2). \tag{3}$$

In (3) h is the monoelectronic part of the total interaction represented in the (χ) AO basis, P is the one-electron density matrix in the (ϕ) MO basis, Z is the bi-electronic part of the interaction and has the following definition in the mixed AO–MO basis for its elements:

$$Z_{pi} = \sum_{jkl} \sum_{qrs} T^\dagger_{js} \langle ps | qr \rangle T_{kq} T_{lr} P_{2klij}. \tag{4}$$

P_2 is the two-electron density matrix in the (Φ) MO basis. The elements of h and Z

have been evaluated under the standard set of INDO approximations and parametrized accordingly.

Equation (1) has been solved iteratively by a variant of the orthogonal gradient method (Golebiewski *et al* 1979; Bhattacharyya and Mukherjee 1979, 1981; Das *et al* 1986b, 1989b). The orbital optimization in this method involves the construction of the following iterative sequence,

$$T_i \rightarrow T_{i+1} = S^{-1} V_i (V_i^\dagger S^{-1} V_i)^{-1/2}. \tag{5}$$

Sometimes iterations based on (5) may end up in divergence. The onset of this divergence may be traced to certain peculiarities in the eigenvalue structure of V and may be handled by a level or root shifting technique recently proposed (Das *et al* 1989a) in the context of MCSCF theory. The geometry optimization has been carried out by a pattern-search method and interpolation involving cubic splines.

3. Quantum chemical valence parameters

The key quantity involved in the definition of the quantum chemical valence parameters is the so-called one-electron density matrix (P) in the AO (χ) basis,

$$P = TP_1 T^\dagger.$$

With the specific choice of $\tilde{\Psi}$ we have made, p can be partitioned into $\bar{P}$ and P^s where $\bar{P}$ represents the part of the one-electron density due to the core or the doubly occupied orbitals and P^s that due to singly occupied orbitals. For the more general MCSCF functions one must use the corresponding natural spin orbitals for defining the P matrix. We can therefore follow Mayer (1983, 1985) and define the bond order between a pair of atoms (A & B) as follows (see also Das *et al* 1986a),

$$B_{ab} = \sum_{\mu \in A} \sum_{\mu \in B} (PS)_{\mu\nu}(PS)_{\mu\nu} + \sum_{\mu \in A} \sum_{\mu \in B} (P^s S)_{\mu\nu}(P^s S)_{\nu\mu}.$$

The free valence on an atom A in the molecule is accordingly given by

$$f_A = \sum_{\mu\nu \in A} (P^s S)_{\mu\nu}(P^s S)_{\mu\nu}.$$

At the INDO level of approximations $S = 1$, leading to the corresponding simplifications of the expressions for B_{AB} & f_A. Somewhat different definitions have been given by Gopinathan and Jug (1983), Gopinathan (1986), Gopinathan and Siddharth (1986) and Siddharth and Gopinathan (1986). We have used an extended version of Mayers definition (Mayer 1986; Das *et al* 1986a). A similar version was earlier used by Villar and Dupuis (1987).

4. Results and discussion

Figures 1a and b display the relevant sections of the PES along the reaction coordinate (the N–H distance, r_{NH}) in the $^3A''$ and $^1A''$ states, respectively. In each case, the molecule is seen to dissociate smoothly into $H(^2s) + NO(^2\pi)$. Apparently no activation barrier is encountered in the reaction path in either of the excited states.
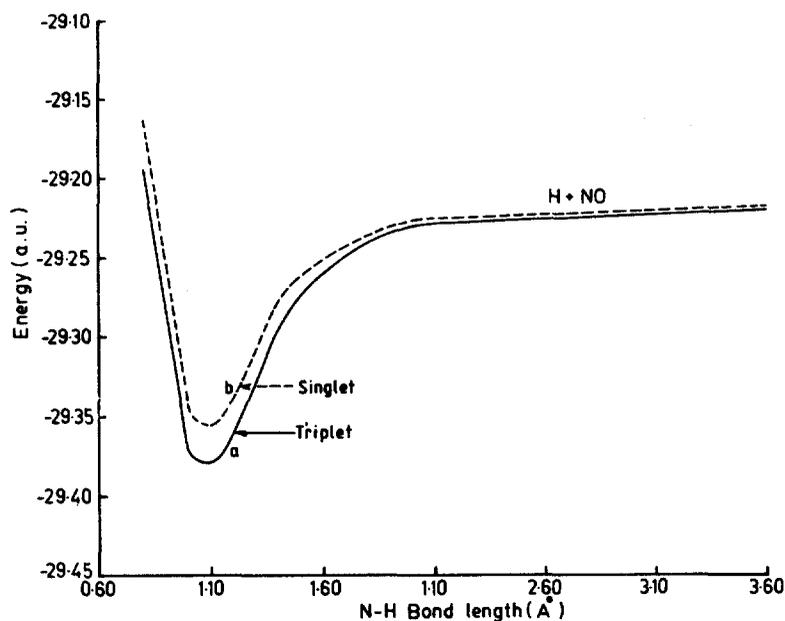
Figure 1. Adiabatic Born–Oppenheimer potential energy curve for the dissociation of $HNO(^3A'') \xrightarrow{hv} H + NO$ (a), and the corresponding singlet curve (b).

However, the energy profiles seem to indicate that the dissociation process occurs over a rather extended region of N–H distances. This is a bit surprising as the rupture of an N–H bond, by analogy with that of a C–H bond in a hydrocarbon, would have been expected to occur more or less sharply at a critical value of N–H bond length. Similar features were observed in *ab initio* calculations as well (Nomura 1980). The singlet and triplet A'' potential energy curves (adiabatic Born–Oppenheimer) cross at a short N–H distance ($r_{NH} < 0.6$ a.u.) while no such crossing is discernible in the long r_{NH} regions. The equilibrium value of the adiabatic singlet–triplet separation is ~ 0.5 eV and the triplet (adiabatic) is predicted to be located ~ 0.2 eV above the singlet equilibrium ground state. Table 1 summarises all the relevant structural data and energies computed by us. These are seen to compare favourably with the available experimental or *ab initio* theoretical data.

Table 2 summarises the changes in the N–O bond length along different points of the adiabatic potential energy curves leading to the dissociation products. The N–O bond distance monotonically decreases as r_{NH} increases and smoothly converges to a value of $r_{NO} \sim 1.16$ Å which is only slightly longer than the N–O length in the ground state. The lowest singlet and triplet A'' states behave identically in this respect. The same table also reports the changes in the H–$\hat{N}$–O angle along the reaction path. From table 2 it appears that H–N–O becomes linear as the N–H bond is stretched beyond $r_{NH} = 1.6$ Å. In the $^1A''$ state, however, the H–$\hat{N}$–O angle does not increase much and remains more or less fixed around $120°$ throughout the course of the photo dissociation process.

Figure 2a depicts the variations in the quantum chemical bond order of the N–H bond (B_{NH}) in the $^3A''$ state along the reaction path. Complete geometry optimization has been carried out at all points of the reaction path. B_{NH} is seen to make a sharp

Table 1. Computed energies and structural data for HNO in the ground and the lowest excited states ($^{1,3}A''$).

Geometrical parameters	Ground state ($^1A'$)		Excited state ($^1A''$)	Excited state ($^3A''$)
r_{NH}(Å)	1·09 1·06[a]	1·04[b]	1·09	1·08 1·06[c]
$\theta_{H\hat{N}O}$ (degree)	111·5 108·5[a]	110·0[b]	102·0	114·5 (110–120)[c]
r_{NO}(Å)	1·19 1·21[a]	1·21[b]	1·23	1·20 1·21[c]
Energy (a.u.)	−29·385835		−29·356140	−29·379615

Quantities superscripted by a, b or c refer to experimental or *ab initio* theoretical data from [a] Herzberg (1966); [b] Peskak *et al* (1971); and [c] Bruna *et al* (1975).

Table 2. Changes in the NO bond length and H–$\hat{N}$–O angle at different points of the reaction path of the photochemical decomposition of

$$HNO(^{1,3}A'') \xrightarrow{h\nu} H + NO.$$
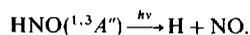
r_{NH}(Å)	r_{NO}(Å)		H$\hat{N}$O (degree)	
	$^1A''$	$^3A''$	$^1A''$	$^3A''$
0·8	1·24	1·21	110·5	126·5
1·0	1·23	1·21	104·5	116·5
1·1	1·23	1·20	101·5	110·5
1·2	1·22	1·20	98·5	110·0
1·3	1·21	1·19	95·5	109·5
1·4	1·17	1·17	101·0	120·0
1·5	1·16	1·16	106·5	128·0
1·8	1·16	1·16	120·0	144·5
2·0	1·16	1·16	120·0	180·0
4·0	1·16	1·16	120·0	180·0

transition from a value of $\sim 1\cdot0$ to $\sim0\cdot0$ through a value of $\sim0\cdot5$ around $r_{NH} = 1\cdot37$ Å. Figure 2b exhibits the hydrogen free valence index (f_H) profile which also reveals a similar transition from a near zero value to unity at $r_{NH} = 1\cdot37$ Å. We conjecture that the point of inflexion in the N–H bond order–bond length plot may be interpreted as the N–H bond rupture point. Figures 3a and 3b depict the corresponding profiles in the $^1A''$ state. The overall features are comparable with what has been observed for the $^3A''$ state. The transition is seen to occur at $r_{NH} = 1\cdot36$ Å. It may therefore be possible

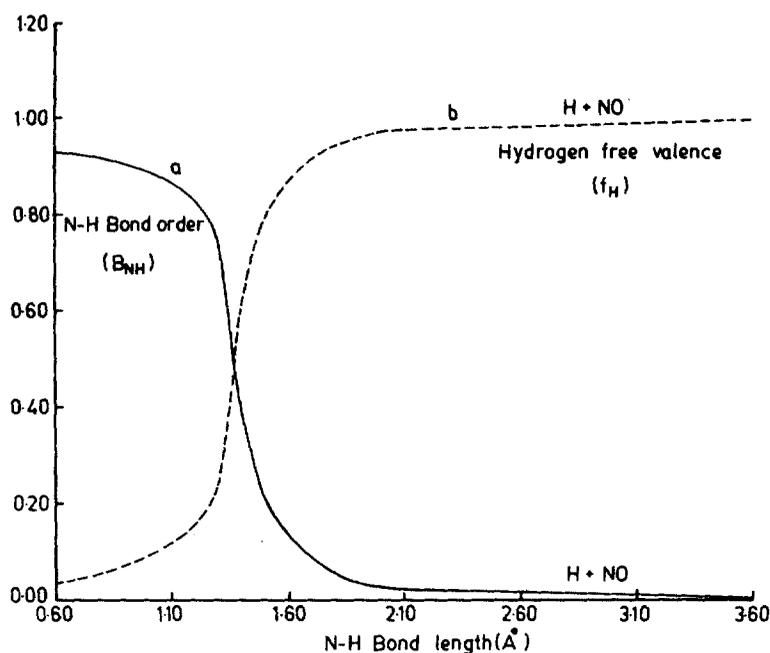**Figure 2.** Variation of N–H bond order (B_{NH}) along the reaction path of the photo-decomposition of $HNO(^3A'') \xrightarrow{h\nu} H + NO$ (a). The corresponding plot (b) for the free valence index (f_H) of the H atom.
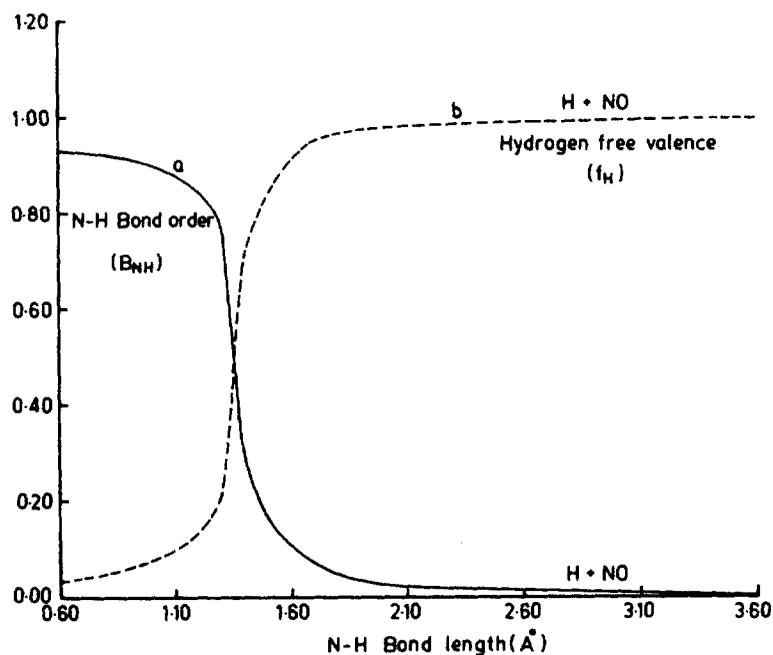

Figure 3. Variation of N–H bond order (B_{NH}) along the reaction path of the photo-decomposition of $HNO(^1A'') \xrightarrow{h\nu} H + NO$ (a). The corresponding profile (b) for the free valence index (f_H) of the H atom.

Table 3. Structural and quantum-chemical valence parameters at the transition point on the reaction path for the photo-decomposition of HNO in the lowest $^{1,3}A''$ states.

Structural and valence parameters	Nature of excited state	
	$^1A''$	$^3A''$
$r_{NH}(\text{Å})$	1·36	1·37
$r_{NO}(\text{Å})$	1·20	1·18
H–N̂–O (degree)	93·5	116·5
B_{NH}	0·69	0·52
f_H	0·30	0·47

to monitor the course of a bond-breaking (and probably bond-making) process by noting the changes in the relevant quantum chemical valence parameters and to locate the bond-breaking point precisely even when the energy profile fails to do that because of the flat character of the PES around the transition region.

Table 3 summarises the structural features and quantum chemical valence parameters at the transition point. The molecule is evidently not linear at this point in either the $^1A''$ or $^3A''$ state. It may appear at first sight that the kind of behaviour observed by us in the changes in bond order (or free valence) along the reaction path is probably fortuitous. We have reasons to believe that it is not so.

Firstly, the idea of using bond order as a key parameter in modelling reactive potential energy surfaces for specific categories of reactions has been successfully tried out in the past. For many systems, surfaces produced by the so-called bond energy–bond order (BEBO) method (see for example Johnston 1960, Johnston and Parr 1963, Marcus 1968, Truhlar 1972, Agmon 1977, Garret *et al* 1982, Dimitrieva *et al* 1986) have many realistic features. BEBO was initially proposed by Johnston (1960) and Johnston and Parr (1963) for collinear reactive triatomic systems representing light atom transfer reactions (viz. A + BC = AB + C) and exploited Paulings bond length–bond order relations (Pauling 1947) together with an empirical formula connecting the bond energy with bond order (or length). With a judicious choice of empirical parameters the BEBO relation has been generally able to model PES well in the vicinity of the minimum energy path. The method has subsequently been further generalised to accommodate non-collinear configurations and regions of the PES away from the minimum energy path. The present study probably indicates that the BEBO method has the possibility of a much broader generalization than originally envisaged and may even have an essentially non-empirical origin. This contention is strengthened by the results of our further investigations on the photo-decomposition and isomerization of X–N–O systems (X–N=O $\xrightarrow{h\nu}$ X + NO and X–N=O $\xrightarrow{h\nu}$ N–O–X) (Maity and Bhattacharyya 1989). We hope to return to the details of these results in the near future.

Acknowledgements

References

Agmon N 1977 *Chem. Phys. Lett.* **45** 343
Bhattacharyya S P and Mukherjee D 1979 *Chem. Phys. Lett.* **66** 511
Bhattacharyya S P and Mukherjee D 1981 *Int. J. Quantum Chem.* **20** 1165
Bruna P J, Kramer W E and Vasudevan 1975 *Chem. Phys.* **9** 91
Bruna P J and Marian C M 1979 *Chem. Lett.* **67** 109
Clyne M A A and Thrush B A 1960 *Discuss. Faraday Soc.* **33** 139
Clyne M A A and Thrush B A 1961 *Trans. Faraday Soc.* **57** 1305
Das K K, Khan P and Bhattacharyya S P 1989a *J. Comput. Chem.* (communicated)
Das K K, Medhi C and Bhattacharyya S P 1986a *Proceedings of the International Seminar on Frontier Areas I*, RRL Jorhat, India (in press)
Das K K, Mukherjee D and Bhattacharyya S P 1986b *Int. J. Quantum Chem.* **29** 1745
Das K K, Mukherjee D and Bhattacharyya S P 1989b *Int. J. Quantum Chem.* **35** 483
Dimitrieva I K, Zenevich Va and Plindor G I 1986 *Chem. Phys. Lett.* **123** 541
Garret B C, Truhlar D G and Magnuson A W 1982 *J. Chem. Phys.* **76** 2321
Golebiewski A, Hinze J and Yurtsever E 1979 *J. Chem. Soc.* 1101
Gopinathan M S 1986 *Proc. Indian Acad. Sci. (Chem. Sci.)* **96** 167
Gopinathan M S and Jug K 1983a *Theor. Chim. Acta* **63** 497
Gopinathan M S and Jug K 1983b *Theor. Chim. Acta* **63** 511
Gopinathan M S and Siddharth P 1986 *Theor. Chim. Acta* **70** 303
Hartley D B and Thrush B A 1967 *Proc. R. Soc. London* **A297** 520
Herzberg G 1966 in *Electronic structure and electronic spectra of polyatomic molecules* (New York: Van Nostrand)
Johnston H J 1960 *Adv. Chem. Phys.* **3** 131
Johnston H J and Parr A C 1963 *J. Am. Chem. Soc.* **85** 2544
Maity D K and Bhattacharyya S P 1989 *J. Am. Chem. Soc.* (submitted)
Marcus R A 1968 *J. Phys. Chem.* **72** 891
Mayer I 1983a *Chem. Phys. Lett.* **97** 270
Mayer I 1983b *Int. J. Quantum Chem.* **23** 341
Mayer I 1985 *Theor. Chim. Acta* **67** 315
Mayer I 1986 *Int. J. Quantum Chem.* **29** 73, 477
McWeeny R 1968 *Faraday Symp. Chem. Soc.* **2** 7
McWeeny R and Mukherjee N G 1970 *Int. J. Quantum Chem.* **4** 97
Nomura O 1980 *Int. J. Quantum Chem.* **18** 143
Pauling L 1947 *J. Am. Chem. Soc.* **69** 542
Peskak J, Klett D S and David E W 1971 *J. Am. Chem. Soc.* **93** 5001
Siddharth P and Gopinathan M S 1986 *J. Mol. Struct. (Theochem.)* **101** 148
Truhlar D G 1972 *J. Am. Chem. Soc.* **94** 7584
Villar H O and Dupuis M 1987 *Chem. Phys. Lett.* **142** 59
Wu A A, Peyrimhoff S D and Buenkar R J 1975 *Chem. Phys. Lett.* **35** 316