

Semiempirical Study of the Interacting Potentials for $H^+ + CO$ and $H^+ + NO^+$

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Recebido em 3 de novembro de 1982; versão revista recebida em 2 de fevereiro de 1984

Abstract Semiempirical INDO molecular orbital calculations of the minimum energy path for the formation of HCO^+ , HOC^+ , HNO^{++} and HON^{++} from the proton reactions $H^+ + CO$ and $H^+ + NO^+$ are presented. Energy barriers, geometry relaxations and stabilization energies are given. Comparisons with ab initio SCF (Self-Consistent Field) and CI (Configuration Interaction) calculations are performed in order to assess the reliability of the calculations.

1. INTRODUCTION

protonation is an interesting problem of increasing research interest. It has been intensively studied in recent years¹⁻¹⁰. An important achievement obtained is that to reproduce existing experimental data on protonation it is of essential importance to consider geometry relaxation. In this vein it has been established that geometry relaxation due to core ionization and protonation on the same site are related^{11,12}. Furthermore their chemical shifts are also correlated^{5,9}. A possible common basis for understanding these relationships may be provided by localized perturbation theory. Therefore the changes of valence electron density upon protonation and core hole formation may be related to older problems describable in terms of atom-atom and bond-atom polarizabilities¹³ as discussed elsewhere¹⁴.

Interest in protonation in diatomic systems has increased, and this is related to ion-molecule reactions occurring in the interstellar space¹⁵. This has led to a number of ab initio calculations of proton reactions^{2,3,7}. An important computational aspect arising from ab initio studies of triatomic radical ions in general is that very poor prediction of the relative stability is obtained at the SCF level.

An interesting example is found for HNO^+ and HON^+ . At SCF with double-zeta basis set it results that HON^+ is the most stable¹⁶. Inclusion of polarization functions in the basis set leads to an almost inexistent barrier¹⁶. The first CI calculation was performed by Marian *et al*¹⁶ and a barrier of 11 kcal/mole was found, with HNO^+ as the most stable. The next CI result is due to McLean *et al*¹⁷, yielding the same trend and a barrier of 13.2 kcal/mole. A very recent CI calculation¹⁸ increased this value to 16.6 kcal/mole. The necessity of including correlation corrections prompts a practical limitation since geometry optimization at ab initio CI level is very expensive. Furthermore, it would become out of reach for most systems of interest. This is particularly the case for a systematic study of proton approach to a realistic molecule.

Most semiempirical methods utilize parameters chosen directly from experiment. Therefore there exists the belief that the model might extend beyond the confinements of the theory. Hence, despite the difficulty in defining correlation energy in a semiempirical scheme, in some cases it may be "built-in". At this stage, there is no concern in separating different energy contributions but obtaining qualitative results directly related to experiment; a modest probe for future investigations on protonation. A systematic calculation of the reactions $\text{H}^+ + \text{CO}$ and $\text{H}^+ + \text{NO}^+$ at the two possible sites will therefore be presented within the semiempirical INDO level¹⁹.

2. PROTONATION OF CO AND NO

The linear HCO^+ and HOC^+ systems have been studied previously at ab initio level by Bruna *et al*³ and Summers and Tyrrell⁷. The latter authors have also studied the double ionized linear products HNO^{++} and HON^{++} . Comparison to their results will be presented below.

Table 1 presents the results and some details for the interacting potential for the reaction $\text{H}^+ + \text{NO}^+ \rightarrow \text{HNO}^{++}$, where HNO^{++} is found to be more stable than the HON^{++} product. For these cases the potential is repulsive in the early stages and becomes attractive in a small region lying energetically above the limit of dissociation into $\text{NO}^+ + \text{H}^+$. Hence, these states are found to be quasibound and unstable upon dissociation in the proton path (see Fig. 1). Our stabilization

Table 1. Geometry, population and energy along the minimum energy path for $H^+ + NO^+ \rightarrow HNO^{++}$

(a)	(b)	(c)	(d)	(e)
$R_{NH} (\text{\AA})$	$R_{NO} (\text{\AA})$	P_H	ΔP_N	E_T (a.u.)
∞	1.1177	0.0	0.0	-27.1491
4.0	1.1177	0.000	-0.042	-27.0285
3.0	1.1177	0.001	-0.068	-26.9935
2.5	1.1176	0.010	-0.087	-26.9708
2.3	1.1174	0.021	-0.093	-26.9629
2.0	1.1169	0.059	-0.090	-26.9581
1.85	1.1167	0.093	-0.079	-26.9621
1.7	1.1164	0.138	-0.061	-26.9725
1.5	1.1163	0.216	-0.022	-26.9964
1.3	1.1161	0.308	+0.031	-27.0239
1.2	1.1162	0.358	+0.061	-27.0309
1.186	1.1162	0.365	+0.066	-27.0310
1.1	1.1165	0.407	+0.094	-27.0245
0.9	1.1174	0.503	+0.162	-26.9197

(a) Fixed. (b) Optimized. (c) Electronic population in the incoming H^+ .
 (d) Change in nitrogen population. (e) Total (valence) energy.

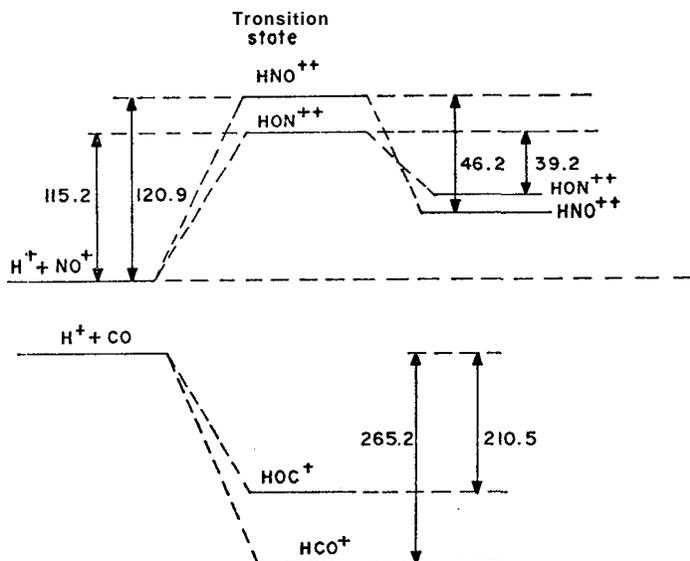


Figure 1 - Energy diagram (kcal/mole). Observe that 1 hartree = 627.7 kcal/mole.

energies (barrier for dissociation) are 46.2 kcal/mole (HNO^{++}) and 39.2 kcal/mole (HON^{++}) and the equilibrium configurations are found to be 75 kcal/mole and 76 kcal/mole above this dissociation limit, respectively. The study by Summers and Tyrrel⁷ on HNO^{++} showed a local minimum with a barrier to dissociation of only 1.7 kcal/mole. Since this value is lower than the zero point energy along the dissociation path, it implies that the system can not be observed even at very low temperatures. Our calculation finds a larger barrier and indicates that the dissociation should proceed by tunneling with an energy release ΔH of about 75 kcal/mole. Table I also shows that the first effect of the proton approach is to polarize the electronic charge of the target system.

The geometrical relaxations are presented in Table 2. The results emphasize the same trend as for core holes, as noticed previously by Palma et al.¹². This same trend is also found regarding relative stabilities of the isomeric products. Protonation in the carbon side gives more stability than in the oxygen side and leads to a decrease of the bond length as compared to the original CO system. These trends could not be verified previously in HNO^{++} and HON^{++} because the solely ab initio calculation found no stability for HON^{++} ⁷. As discussed in the introduction, this result is probably due to the absence of correlation. In agreement with the above discussed trend we find here that protonation on the nitrogen leads to a small shortening of the bond distance and is the most stable (see fig. 1).

Table 2. Geometrical Relaxation (Å)

	R_{CO}		R_{NO}
CO	1.196	NO^+	1.118
HCO^+	1.181	HNO^{++}	1.116
HOC^+	1.214	HON^{++}	1.130

The relative stability of HCO^+ over its isomer is found as 54.7 kcal/mole as compared to 18.8 kcal/mole³ and 21.7 kcal/mole⁷. This result indicates that the preferable protonation site is cor-

rectly described but the proton affinities are overestimated. We find it to be about 260 kcal/mole as compared to about 140 kcal/mole as obtained by Forsen and Roos²⁰. The energy picture is summarized in figure 1.

In agreement with the accurate CI calculations of Bruna *et al*³ we find no barrier for the protonation of CO to form either COH⁺ or HCO⁺. This is indicative of the qualitative reliability of the interacting potential as an initial SCF calculation leads to a spurious barrier⁷ for the formation of HCO⁺.

3. SUMMARY

The proton reactions H⁺ + CO and H⁺ + NO⁺ producing the triatomic linear systems HCO⁺, HOC⁺, HNO⁺⁺ and HON⁺⁺ have been studied within the semiempirical INDO level. Comparison with existing data leads to good overall agreement. The results reproduce the expected trends. The interacting potential for the reactions were obtained and analyzed. The results for the HNO⁺⁺ is interesting insofar as we obtain it as an unstable system under proton dissociation but this reverse process should occur by tunneling. More accurate calculations is hereby suggested to clarify this point.

Finally, the insight gained in this pilot study will hopefully be used in a more general study of proton reactions in larger molecules.

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Resumo

Cálculos de orbitais moleculares no modelo semi-empírico INDO são feitos para estudar a formação de HCO^+ , HOC^+ , HNO^+ e HON^+ a partir do processo de protonação $\text{H} + \text{CO}$ e $\text{H} + \text{NO}$ ao longo da trajetória de menor energia. Barreiras de energia, relaxações geométricas e energias de estabilização são dadas. comparações com cálculos ab initio SCF (Self-Consistent Field) e CI (Configuration Interaction) são feitas para avaliar os resultados.