Test of a Kinetics Scheme: Emission in H(^{2}S) + NO($^2\Pi$)*

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The mechanism to explain the afterglow in the collision of H(^{2}S) and NO($^2\Pi$) is critically examined by calculating part of the energy surface of the ^{3}A″ state. It is found that the long range interaction energies are consistently repulsive even though at shorter distances attractive ionic interactions dominate. It is concluded that the essential feature of the Clyne and Thrush mechanism is missing; intimate interaction of H(^{2}S) and NO($^2\Pi$) is not possible at room temperature along the ^{3}A″ surface. This study was undertaken to provide an example where a theoretical calculation is required to critically test a kinetics mechanism.

Key words: Hartree-Fock; HNO(^{1}A′, ^{3}A″, ^{1}A′); interaction energy; ionic state; radiative recombination; reaction barrier.

1. Introduction

The understanding of the kinetics of reaction often depends upon a knowledge of the energy surface or surfaces accessible to the reactants. When theoretical information is lacking, the available experimental information is often used to construct a schematic representation. A particular example of this is seen in the mechanism proposed by Clyne and Thrush [1] to explain the afterglow in the collision of H(^{2}S) and NO($^2\Pi$). Four molecular states correlate with these asymptotic fragments. There is a X^{1}A′ ground state and ^{3}A″, ^{1}A″, and ^{3}A′ excited states. The ^{1}A″ is known [2] to have a considerable barrier to the interaction of H and NO. Clyne and Thrush therefore proposed that the rate determining step is a radiationless transition

$$\mathrm{HNO}(^3\mathrm{A}'') \rightarrow \mathrm{HNO}(^1\mathrm{A}'')$$
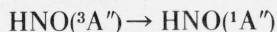
which is followed by

$$\mathrm{HNO}(^1\mathrm{A}'') \rightarrow \mathrm{HNO}(^1\mathrm{A}') + h\nu.$$

No barrier is presumed to impede the close approach of H and NO in the continuum of the ^{3}A″ state. The ^{3}A″ state provides a path for an intimate collision and ultimate curve crossing to the ^{1}A″.

This study will directly test this mechanism by determining the ^{3}A″ energy surface especially at large interfragment distances. The ^{3}A″ energy surface will be calculated in the H.F. approximation [3]. Asymptotically only one configuration will determine the energy behavior since the H.F. wave function behaves correctly as the fragments separate. At shorter distances there is no low lying excited state that can qualitatively modify the H.F. surface. Since we are looking for a yes-no answer the qualitatively correct H.F. surface will suffice.

2. Hartree-Fock Calculation

The Gaussian-type function (GTF) basis is obtained from Huzinaga [4]. A contracted set of the 9s and 5p atom GTF basis is used for N and O and three s GTF are used for the H atom. The NO internuclear distance is fixed at 2.1747 a.u. which is the X$^2\Pi$ ground state equilibrium value. The H atom approaches the NO molecule along four lines. Two are collinear. The H atom approaches from the N or O side. The main calculation effort is along a line which is directed at the N atom and at an angle of 110°. Points along this line will be close to the equilibrium geometry of the ^{1}A′ and ^{1}A″ states. Two points were calculated on a line between the H and O atoms with an angle of 150°. Cost will not permit a more complete determination of the surface. Nontheless the results in table 1, which are illustrated in figure 1, are sufficient to test the Clyne and Thrush mechanism.

One of the features of the calculations at 110° is the sudden change of wave function when R(NH) is about 3.0 a.u. Nonetheless the H.F. equations still converged smoothly although somewhat slowly to a solution. For linear encounters of H with O at 150° the convergence proved to be extremely slow but the barrier at 110° is duplicated on the 150° line.

FIGURE 1

TABLE 1. *Calculated interaction energies for* H + NO

Linear	$E - E_\infty$ (a.u.)		
R(HN)	$^3\Pi$	$^1\Delta$	$^3\Sigma^-$
2.	0.1673	0.0535	0.0110
4.	.0088		
5.	.0016		
6.	.0002		
R(HO)			
3.5	0.0137		
4.	.0050		
4.3	.0034		
4.5	.0024		
5.0	.0009		

110° < HNO

R(HN)	$^1A'$	$^1A''$	$^3A''$
1.6			0.0147
1.8			−.0166
2.0	−0.0363	0.0141	−.0211
2.2			−.0132
3.0			.0209
4.0			.0051

150° < HON

R(HO)			$^3A''$
3.0			0.0279
4.5			.0011

For sake of comparison, the ground state X^1A' with a configuration

$$1a'^2\,2a'^2\,3a'^2\,4a'^2\,5a'^2\,6a'^2\,1a''^2\,7a'^2, X^1A'$$

was calculated as well as the $^1A''$ in which, analogously to the $^3A''$, the $7a'$ orbital is excited to a $2a''$. In addition to the $^3\Pi$ two other states were calculated for the linear HNO conformation, the $^1\Delta$ and $^3\Sigma^-$. All of these states were calculated for R(HN) equal to 2.0 a.u. which is close to the observed [5] internuclear distance in the ground state HNO.

3. Conclusion

When the H(^{2}S) and NO($^2\Pi$) interaction is collinear only $^3\Pi$ and $^1\Pi$ molecular states will arise. In the H.F. approximation the $^1\Pi$ is almost invariably above the $^3\Pi$ state so calculation of the $^3\Pi$ will determine the character of both states. The approach from the N side yields a repulsive curve even to the close approach of R(HN) equal to 2.0 a.u. At this distance the $^1\Delta$ and $^3\Sigma^-$ states are much more stable but in a linear correlation they can not dissociate to ground state fragments. From the O side the interaction curve is also repulsive. At R(HO) equal to 3.5 a.u. the repulsion energy is already 0.35 eV.

Along the 110° line the barrier height for the $^3A''$ reaches about 0.6 eV which certainly precludes penetration for all but very energetic H atoms. At R(HN) equal to 3.0 a.u. the wave function suddenly changes character. The $7a'$ orbital which is primarily a H 1s function shifts charge to the NO Π type functions. The total wave function at R(HN)=2.0 a.u. is best described as a predominately ionic interaction between an H$^+$ and a NO$^-$. At this point the $^3A''$ is 0.6 eV stable relative to the asymptotic fragments. The $^1A''$ is almost 1.0 eV above the $^3A''$ at this point or about 0.4 eV above the asymptote. Correlation energy can be large in this case since all the open shell orbitals are valence in character and penetrate the closed shell core. The extent to which the correlation and H. F. errors cancel is difficult to estimate. But it is clear [2] that the $^1A''$ has a minimum 0.45 eV below the asymptote since there is no activation energy for the emission. If the $^1A''$ is displaced downward by 0.85 eV and the $^1A'$ by about 1.1 eV then the observed excitation energy and dissociation energies are satisfied. Such values are consonant with electron-pair correlation energies but in this case are an amalgam of correlation and H.F. errors.

The maximum observed in the $^3A''$ along the 110° line will be relatively unaffected by the correlation energy since the ionic charge transfer has not yet occurred. Since the $^1A''$ barrier is expected to remain above the $^3A''$ at these distances, the observation of vibrational bands well above the dissociation limit is expected.

The approach along the H−O line also exhibits a barrier that is at least 0.6 eV high. This barrier is again sufficient to preclude penetration.

The barriers that are calculated on all four lines of approach of the H atom are representative of the $^3A''$ Hartree-Fock energy surface. It is difficult to envisage another result for any other angle of attack. From the present results one would be reluctant to consider the $^3A''$ surface as an important path for the population of $^1A''$ HNO molecules. It should be noted that radiationless transitions could occur from vibrationally excited X^1A' or even from the continuum of X^1A' which is the one remaining bimolecular pathway that is energetically accessible.
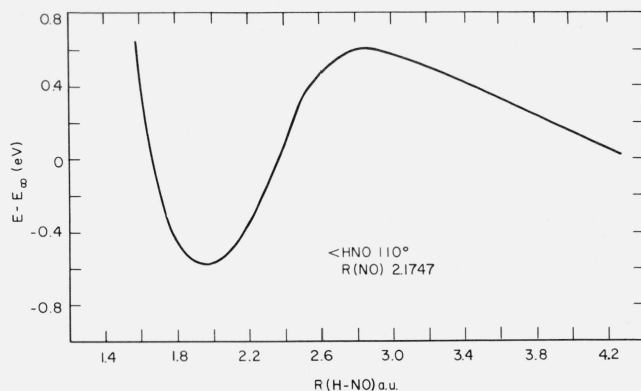
4. References

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