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Potential Energy Surfaces for Ion-Molecule Reactions. Intersection of the $^3A_2$ and $^2B_1$ Surfaces of NH_2^+

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Abstract

The $N^+ + H_2$ system is one of the few ion-molecule reactions for which detailed molecular beam studies have been carried out. To complement this experimental research, we have performed a theoretical study of two of the low-lying NH_2^+ potential energy surfaces. The intersection and avoided intersection (for C_s geometries) of the lowest $^3A_2$ and $^3B_1$ surfaces allows a pathway by which the ground state of NH_2^+ may be accessed without a potential barrier. The electronic structure calculations employed a double zeta plus polarization basis set, and correlation effects were taken into account using the newly developed Vector Method (VM). To test the validity of this basis, additional self-consistent-field studies were performed using a very large contracted gaussian basis N(13s 8p 3d/9s 6p 3d), H(6s 2p/4s 2p). The $^3A_2$ surface, on which N^+ and H_2 may approach, has a surprising deep potential minimum, ∿ 60 kcal/mole, occurring at r_e(NH) ∿ 1.26 Å and θ_e(HNH) ∿ 43°. Electron correlation is responsible for about 15 kcal of this well depth, which appears fairly insensitive to extension of the basis set beyond the double zeta plus polarization level. The line of intersection (or seam) of the $^3A_2$ and $^3B_1$ surfaces is presented both numerically

and pictorially. The minimum energy along this seam occurs at $\sim$ 51 kcal below separated $N^+ + H_2$. Thus for sufficiently low energies one expects $N^+ - H_2$ collisions to provide considerable "complex formation". Further molecular beam experiments at such low energies (< 0.5 eV) would be of particular interest.

Introduction

Simple ion-molecule reactions have provided some of the most fascinating examples to date of the interplay between different potential energy surfaces of a single chemical system[1]. Most noteworthy in this regard are the molecular beam studies of Mahan and coworkers[2-4], who have carefully investigated, among other systems, the $C^+ + H_2$, $N^+ + H_2$ and $O^+ + H_2$ reactions. These reactions are particularly appealing as prototypes, since they are sufficiently simple to be studied by both electronic structure theory[5] and classical[6] or semiclassical[7] dynamics. In addition, the use of qualitative electronic correlation diagrams[1,8] has also proven very helpful in understanding these simple reactions, and alternatively the experiments may serve as testing grounds for simple molecular orbital theory.

A reasonable starting point for our discussion is the $N^+ + H_2$ electronic state correlation diagram of Fair and Mahan[3]. This diagram is reproduced with their permission in Figure 1. As discussed by Fair and Mahan (and elsewhere[9,10] in regard to the $C^+ + H_2$ reaction) the key feature in the interpretation of low energy (say less than ∿ 3 eV) molecular beam results is the intersection of two low-lying potential energy surfaces. For the $N^+ + H_2$ case (in C_{2v} symmetry) these are the $^3B_1$ and $^3A_2$ surfaces. The $^3B_1$ state is known[11-14] to be the ground state of NH_2^+, the nitrenium ion, while the $^3A_2$ state is less understood. However, on the basis of orbital symmetry considerations[1,8] and earlier theoretical work[9] on $C^+ + H_2$, the $^3B_1$ surface is expected to be quite repulsive as the N^+ initially approaches H_2. The deep well of the $^3B_1$ surface is "protected" from $N^+ - H_2$ collisions on the same surface by means of this large barrier. However, the $^3A_2$ surface should be either much less repulsive[9] or attractive[10] as N^+ approaches H_2. And since the two surfaces are both of $^3A''$ symmetry as soon as the N^+ ion moves off the H_2 perpendicular bisector, the C_{2v} crossing of surfaces becomes an avoided intersection. If there are points along this crossing of $^3B_1$ and $^3A_2$ surfaces which lie at energies near or below the $N^+ + H_2$ asymptote, then there exists a barrier-free pathway

$$^3A_2 \rightarrow {}^3A'' \rightarrow {}^3B_1 \qquad (1)$$

for the formation of ground state NH_2^+ from separated N^+ plus H_2. Such a pathway for the analogous situation with respect to $C^+ + H_2$ has been recently demonstrated unequivocally in the important theoretical work of Pearson and Roueff[10].

In their communication Pearson and Roueff[10] bring to light a critical ingredient in the proper theoretical treatment of this problem. That is, polarization functions[5] (d functions on carbon and p functions on the hydrogen atoms in their case) critically affect the energy at which the seam or line of intersection occurs. Their finding is pertinent to the present discussion since Gittins and Hirst[15] have recently reported single configuration self-consistent-field (SCF) results for $N^+ + H_2$ using a basis set which is quite well-chosen and flexible[16,17] but lacks polarization functions. Gittins and Hirst conclude that access to the deep $^3B_1$ potential well may be possible with only a small barrier, on the order of 4 kcal/mole. By comparison of the effects of polarization functions in the $C^+ + H_2$ system[9,10], it would appear likely that this barrier should disappear completely. The present paper, then, builds on the Gittins-Hirst work[15] but goes well beyond it for the $N^+ + H_2$ system by the use of larger basis sets and the direct inclusion of correlation effects. These two theoretical extensions should allow for a meaningful comparison with the molecular beam experiments of Fair and Mahan[3].

Theoretical Approach

Two basis sets of contracted gaussian functions[5,17] were used here. The first was a standard Huzinaga-Dunning double zeta plus polarization (DZ + P) set, designated N(9s 5p 1d/4s 2p 1d), H(4s 1p/2s 1p). The polarization function exponents were 0.8 (nitrogen d functions) and 1.0 (hydrogen p functions), and a scale factor of $\zeta = 1.2$ was used on the hydrogen s functions. This first basis is essentially the same (except for the obvious replacement of the C basis by one appropriate to N) as that used by Pearson and Roueff[10], and was used for both SCF and configuration interaction (CI) calcuations.

Since we were initially quite surprised by Pearson and Roueff's demonstration[10] of the critical importance of polarization functions, it was decided to carefully test whether further extensions of their basis would be of qualitative importance to the shape of the $N^+ + H_2$ potential surfaces. Therefore, following the recent work of Meadows[18] on CH_2, a very large basis was adopted: N(13s 8p 3d/9s 6p 3d) and H(6s 2p/4s 2p). The polarization functions had gaussian orbital exponents $\alpha = 1.6, 0.8$, and 0.3 for the nitrogen d functions and $\alpha = 1.4$ and 0.25 for the hydrogen p functions based on past experience[5,19-23]. The nitrogen sp functions and hydrogen s functions were the appropriate primitive gaussian basis sets of van Duijneveldt[22], contracted to provide maximum flexibility in the valence region. That is, the five s functions with largest orbital exponents α_i were grouped together according to the nitrogen atomic 1s orbital, and an analogous procedure followed for the three nitrogen p functions with largest exponents. Based in part on Clementi and Popkie's study[23] of the water molecule with many basis sets, we estimate that the present basis set for NH_2^+ should yield total energies within 0.005 hartrees (∿ 3 kcal) of the Hartree-Fock limits for the $^3A_2$ and $^3B_1$ potential surfaces. Relative errors, of course, should be much smaller.

The electron configuration for the two states of primary interest are

$$1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1\ 1b_1 \qquad {}^3B_1 \qquad (2)$$

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 1b_2\ 1b_1 \qquad {}^3A_2 \qquad (3)$$

and restricted SCF theory[24,25] has been applied to both of these states. We also note that the first excited electronic state of NH_2^+ is of $^1A_1$ symmetry and several two-configuration

$$\begin{array}{l} C_1\ 1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1^2 \\ +\ C_2\ 1a_1^2\ 2a_1^2\ 1b_2^2\ 1b_1^2 \end{array} \qquad {}^1A_1 \qquad (4)$$

SCF studies of this state were also made. Finally, it should be noted that the source of the large barrier in the $N^+ + H_2$ $^3B_1$ approach is the fact that for large $N^+ - H_2$ separations the

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 1b_1\ 4a_1 \qquad {}^3B_1 \qquad (5)$$

configuration, rather than (2), dominates the wave function.

A number of direct SCF comparisons of the two basis sets were made. Here we report two such tests, the first with the N^+ and H_2 species separated by a distance R = 100 bohr radii. R is the distance between the N^+ ion and the H_2 bond midpoint, while r will designate the H-H internuclear separation. For R = 100, r = 1.4 (essentially the equilibrium internuclear separation of H_2) the $^3A_2$ SCF energies are -55.01159 and -55.02123 hartrees, the difference being 0.00964 hartrees or 6.0 kcal/mole. Secondly we report a point near the equilibrium $^3A_2$ geometry, namely R = 2.0 and r = 1.8 bohr, where the two basis sets yield SCF energies -55.07823 and -55.09157 hartrees. The difference in the latter case is somewhat larger, 0.01334 hartress or 8.4 kcal/mole. It is certainly not suprising that the near Hartree-Fock basis yields somewhat lower relative energies as N^+ and H_2 approach. And if SCF basis set errors are directly transmitted to CI results, one would expect our DZ + P basis to yield CI dissociation energies for N^+ - H_2 about 2.5 kcal less than the exact values. Of course, in the present case, the uncertainties in our treatment of the correlation problem are roughly of that same order of magnitude. In any case the potential surface differences arising from the two basis sets are small, about an order of magnitude less than those found by Pearson for CH_2^+ in going from the DZ to the DZ + P basis set.

Electron correlation was taken into account variationally using the newly developed vector method (VM) of Bender and coworkers[26]. The CI calculations were carried out with the early version of the VM code. That is, all Slater determinants differing by one or two spin orbitals from (2) for the $^3B_1$

calculations or (3) for the $^3A_2$ calculations were included. In this way 1840 and 1824 determinants were respectively employed in the $^3B_1$ and $^3A_2$ variational procedures. The above was carried out with the usual restriction that the $1a_1$ orbital (essentially nitrogen 1s) be doubly occupied in all determinants. It is now well-established[5] that such a CI procedure will provide at least 90% of the attainable valence shell correlation energy in cases (such as the present) where the wave function is qualitatively described by a single determinant SCF wave function.

Use of the near Hartree-Fock basis was restricted to the location of the equilibrium geometries of the $^3A_2$, $^3B_1$, and $^1A_1$ electronic states. With the DZ + P basis, a regular grid of points (available from the authors on request) for both the $^3B_1$ and $^3A_2$ states was mapped out. These were all combinations of $R = 3.0$, 2.5, 2.0, 1.75, 1.5, and 1.25 bohrs with $r = 1.2$, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, and 2.6 bohrs for a total of $6 \times 8 = 48$ points on the surface. To provide a reference point for the relative energies quote hereafter, we note that for the $^3A_2$ state $R = 100$, $r = 1.4$, the SCF and CI energies with the DZ + P basis were -55.01158 and -55.12329 hartrees. Thus for separated N^+ plus H_2 the calculated correlation energy is 0.111708 hartrees. As we will see, the correlation energy increases as the N^+ and H_2 are brought together.

Singlet-Triplet Separation in the Nitrenium Ion

Before going on to the primary purpose of this research, let us take a brief digression. Although the $^3B_1$ - $^1A_1$ separation in NH_2^+ is not known experimentally, there have been at least four theoretical predictions of this quantity. On the *ab initio* side the groups of Morokuma[11], Hayes[12], and Harrison[13] have predicted 45, 36, and 45 kcal/mole, with the $^3B_1$ state the lower lying in each case. More recently Haddon and Dewar[14] have used their semi-empirical MINDO/3 method to predict 31 kcal for this quantity.

For comparison with these results, the near Hartree-Fock basis was used to predict the $^3B_1$ and $^1A_1$ equilibrium geometries. For the $^3B_1$ state the predicted structure was $r_e(NH) = 1.018$ Å, $\theta_e(HNH) = 143.3°$, corresponding to a total SCF energy of -55.22965 hartrees. The two-configuration SCF description (4) of the $^1A_1$ state yields $r_e(NH) = 1.033$ Å, $\theta_e(HNH) = 108.2°$ and a total energy of -55.18329 hartree. Thus the singlet-triplet separation ΔE is predicted to be 0.04636 hartrees = 29.1 kcal/mole.

The best means of evaluating the reliability of the above prediction is by comparison of analogous theoretical procedures with experiment for CH_2, for which an accurate ΔE ($^3B_1$ - $^1A_1$) has recently become available[27]. The experimental value of 19.5 ± 0.7 kcal may be compared with the 10.9 kcal obtained[18] for CH_2 by the method described in the previous paragraph. Thus it is evident that a two-configuration description of the $^1A_1$

state overcompensates for the fact that the $^3B_1$ state has less correlation energy. For CH_2 the use of a single configuration SCF treatment of the $^1A_1$ state yields a separation of 24.8 kcal, too large as expected. More precisely the experimental result lies 61.9% of the way from the two-configuration $^1A_1$ result to the one-configuration $^1A_1$ result.

With the above in mind, we carried out single configuration ($1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1^2$) SCF calculations on NH_2^+, yielding r_e(NH) = 1.032 Å, θ_e(HNH) = 109.6°, and E = -55.15838. The singlet-triplet separation obtained in this way (44.7 kcal) is considerably greater than the two-configuration result, 29.1 kcal. It seems quit certain that the exact nitrenium separation lies between the two, and if the same 61.9% criterion is used, a semi-empirical prediction of 38.8 kcal is made. Partly because of the semi-empirical nature of our prediction and also because of the use of a Hartree-Fock limit basis, we suggest that the 38.8 kcal value is probably the most reliable prediction made to date.

Region of Intersection of the $^3A_2$ and $^3B_1$ Surfaces

Certainly the most interesting result found here is the rather deep potential well associated with the $^3A_2$ state of NH_2^+. Such a deep well is not anticipated from the $C^+ - H_2$ calculations of Liskow, Bender and Schaefer[9] or the correlation diagram (Figure 1) of Fair and Mahan. Such a well is implicit in the work of arson[10], but he does not report the predicted $^2B_2$ (analogous to the NH_2^+ $^3A_2$ state) dissociation energy relative to separated $C^+ + H_2$. We do know that Pearson's CH_2^+ $^2B_2$ state must be bound by at least 15 kcal, since that is the lowest energy at which the $^2B_2$ and $^2A_1$ electronic states are degenerate.

Using the near Hartree-Fock basis, the $^3A_2$ state of NH_2^+ is predicted by SCF theory to have an equilibrium geometry $r_e(NH) = 1.207\text{Å}$, $\theta_e(HNH) = 46.4°$. This small bond angle is characteristic of the early approach of N^+ to H_2; and the predicted equilibrium geometry corresponds to a near Hartree-Fock energy 44.6 kcal below separated N^+ plus H_2. Using the DZ + P basis the $^3A_2$ minimum is less precisely located since the grid (see previous section) is relatively sparse in this region (note that the density of grid points is greatest near the intersection of the $^3A_2$ and $^3B_1$ surfaces). With this disclaimer we note that the DZ + P SCF minimum is predicted by a 9-point fit to lie at $r_e(NH) = 1.25$ Å, $\theta_e = 42°$, with energy 44.3 kcal below separated $N^+ + H_2$. Realistically the true SCF minimum with this basis probably occurs about 2 kcal higher, when one considers the direct comparisons (between DZ+P and near Hartree-Fock basis sets) of the previous section. Similarly the CI equilibrium geometry is $r_e(NH) = 1.26$ Å, $\theta_e = 43°$, and lies 60.4 kcal below $N^+ + H_2$.

The lowest actual calculated point on the $^3A_2$ surface occurs at $R = 2.0$ bohrs, $r = 1.8$ bohrs (or $r(NH) = 1.161$ Å, $\theta = 48.5°$) for both SCF and CI methods. These points lie 41.8 and 56.8 kcal below the comparable asymptotic calculations and make it quite clear that electron correlation contributes $\sim$ 15 kcal to the well depth. If in turn this 15 kcal is added to the near Hartree-Fock well depth of 44.6 kcal, one obtains 59.6 kcal as the predicted dissociation energy relative to $N^+ + H_2$. In any case a value of ∿ 60 kcal for the dissociation energy consistently appears on the basis of the present theoretical research. A dissociation energy this large (nearly 3 eV) must be considered surprising as it certainly cannot be justified in terms of a classical electrostatic picture.

The $^3A_2$ and $^3B_1$ surfaces are illustrated in Figures 2 and 3. Note, of course, that since the region of interest here is that near the intersection, the actual position of the $^3B_1$ NH_2^+ equilibrium geometry is not included. The fact that the $^3B_1$ surface becomes very attractive in that direction is however quite clear. Also apparent is the large barrier (∿ 75 kcal) associated with the Woodward-Hoffmann forbidden[8] least motion[9] insertion of N^+ into H_2. To complement the two contour maps and the line of intersection indicated on each, Table I gives some numerical values for the line of intersection.

It seems quite clear from previous work[9,10] on the related C^+ - H_2 system that the C_{2v} approach along the $^3A_2$ surface is by far the most likely to lead to the bound NH_2^+ species. In this light one can make a rough picture of one important aspect of the dynamics. First, as Figure 2 implies, high energy C_{2v} collisions will tend to be unreactive.[3] That is, with r(H-H) fixed at 1.4 bohrs, the $^3A_2$ surface becomes quite repulsive rather quickly. For example, at R = 1.5 bohrs the surface lies 35 kcal above separated $N^+ + H_2$. Therefore a key feature leading to complex formation is the necessity that the collision occur slowly enough that the H-H separation can become sufficiently large to reach the area of the line of intersection. Inspection of Figures 1 and 2 or Table I shows that the line of intersection reaches zero kcal relative energy at about $R \approx 1.52$ bohrs, $r \approx 1.67$. In other words the H-H separation must increase by nearly 0.3 bohrs ∿ 0.15 Å for the line of intersection to become dynamically meaningful in low energy collisions.

A final noteworthy point is that the line of intersection for the $N^+ - H_2$ system passes through much lower relative energies (50 kcal vs 15 kcal) than the corresponding line of intersection for the $C^+ - H_2$ system.[10] A naive interpretation of this comparison would suggest that at low energies one should observe more complex formation for the N^+ than the C^+ reaction. At this point, however, we believe that detailed dynamical studies are called for. This work on $N^+ - H_2$ and Pearson's research[10] for $C^+ - H_2$ appear to provide rather accurate predictions of some of the crucial potential surface features, and the greatest uncertainties are now of a dynamical nature. Of course, more information concerning these surfaces would be welcome, especially concerning the slopes of the two lowest $^3A''$ surfaces (arising from $^3A_2$ and $^3B_1$ in C_{2v} point group) in the region of their avoided intersection.

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Table I. Line of intersection of the lowest $^3A_2$ and $^3B_1$ potential energy surfaces of NH_2^+. These points are given in two coordinate systems for ease of interpretation. As noted in the text, R is the distance between the N^+ nucleus and the H_2 bond midpoint. Energies are configuration interaction (CI) energies relative to separated $N^+ + H_2$.

R(bohrs)	r(bohrs)	r(N-H) Å	θ(HNH) degrees	Energy (kcal/mole)
1.30	1.240	0.762	51.0	171.0
1.35	1.330	0.796	52.4	116.6
1.40	1.425	0.831	53.9	72.6
1.45	1.523	0.867	55.4	37.6
1.50	1.623	0.902	56.8	10.4
1.55	1.726	0.939	58.2	-10.4
1.60	1.834	0.976	59.6	-26.1
1.65	1.946	1.014	61.1	-37.3
1.70	2.061	1.052	62.4	-44.7
1.75	2.179	1.091	63.8	-49.1
1.80	2.301	1.130	65.2	-51.0
1.85	2.426	1.171	66.5	-50.8
1.90	2.556	1.212	67.9	-48.8

FIGURE CAPTIONS

Figure 1. Correlation diagram of Fair and Mahan[3] for the $N^+ - H_2$ system.

Figure 2. $^3A_2$ potential energy surface for NH_2^+. R(N-CM) is the distance from the nitrogen nucleus to the H_2 center of mass. Contours are labeled in kcal/mole relative to infinitely separated N^+ plus H_2. Note that contours energetically below 25 kcal are labeled in 5 kcal intervals, while those above 25 kcal are spaced by 25 kcal.

Figure 3. $^3B_1$ potential energy surface for NH_2^+. R(N-CM) is the distance from the nitrogen nucleus to the H_2 center of mass. Contours are labeled in kcal/mole relative to infinitely separated N^+ plus H_2. Note that contours energetically below 25 kcal are labeled in 5 kcal intervals, while those above 25 kcal are spaced by 25 kcal.

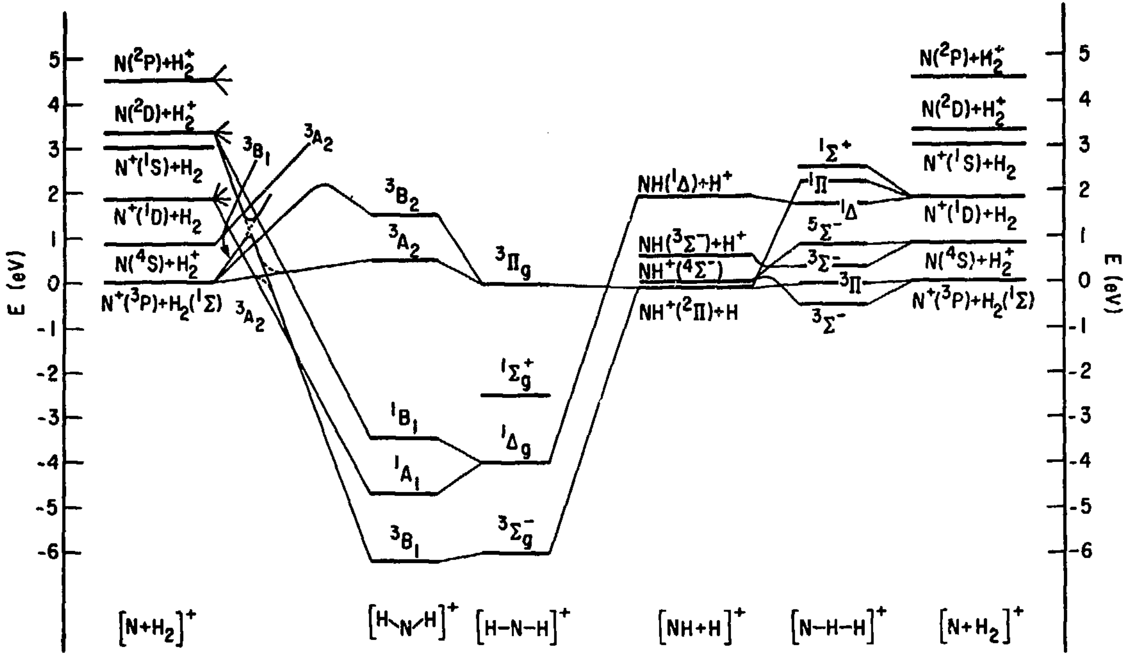
E (eV)
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
N(²P)+H₂⁺
N(²D)+H₂⁺
N⁺(¹S)+H₂
N⁺(¹D)+H₂
N(⁴S)+H₂⁺
N⁺(³P)+H₂(¹Σ)
³B₁
³A₂
³A₂
³B₂
³A₂
³B₁
¹B₁
¹A₁
³Πg
¹Σg⁺
¹Δg
³Σg⁻
NH(¹Δ)+H⁺
NH(³Σ⁻)+H⁺
NH⁺(⁴Σ⁻)
NH⁺(²Π)+H
¹Σ⁺
¹Π
¹Δ
⁵Σ⁻
³Σ⁻
³Π
³Σ⁻
N(²P)+H₂⁺
N(²D)+H₂⁺
N⁺(¹S)+H₂
N⁺(¹D)+H₂
N(⁴S)+H₂⁺
N⁺(³P)+H₂(¹Σ)
E (eV)
[N+H₂]⁺
[H\N/H]⁺
[H–N–H]⁺
[NH+H]⁺
[N–H–H]⁺
[N+H₂]⁺

Figure 1

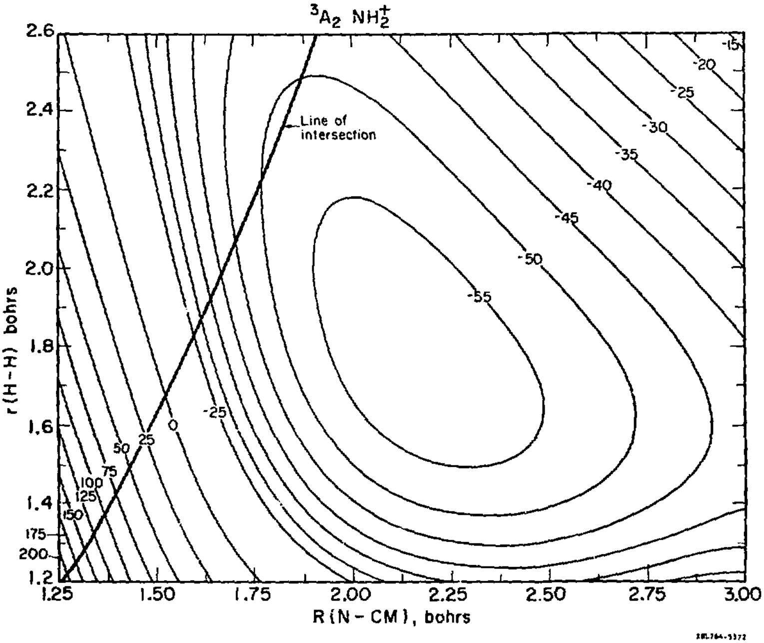
³A₂ NH₂⁺
r(H-H) bohrs
R(N - CM), bohrs
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.25
1.50
1.75
2.00
2.25
2.50
2.75
3.00
Line of intersection
-15
-20
-25
-30
-35
-40
-45
-50
-55
-25
0
25
50
75
100
125
150
175
200
XBL 764-5372

Figure 2

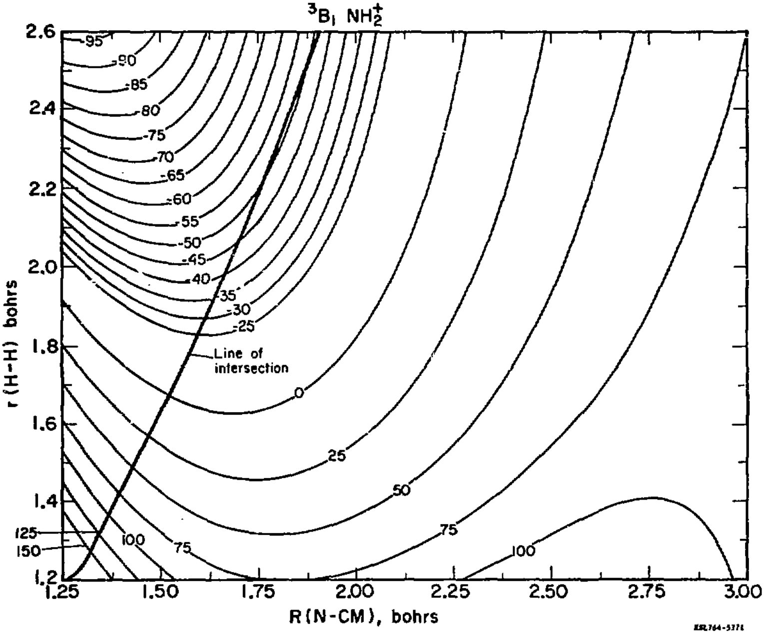
$^3B_1$ NH$_2^+$
-95
-90
-85
-80
-75
-70
-65
-60
-55
-50
-45
-40
-35
-30
-25
Line of intersection
0
25
50
75
100
125
150
100
75
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
r(H-H) bohrs
1.25
1.50
1.75
2.00
2.25
2.50
2.75
3.00
R(N-CM), bohrs
XBL764-5378

Figure 3