

Ab initio Study of the $\text{NH}_3 \cdots \text{H}_2$ Complex – First Saddle Point of Index Two on a Reaction Path

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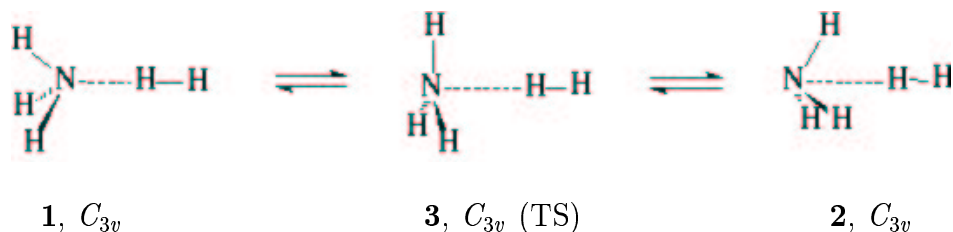
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Abstract

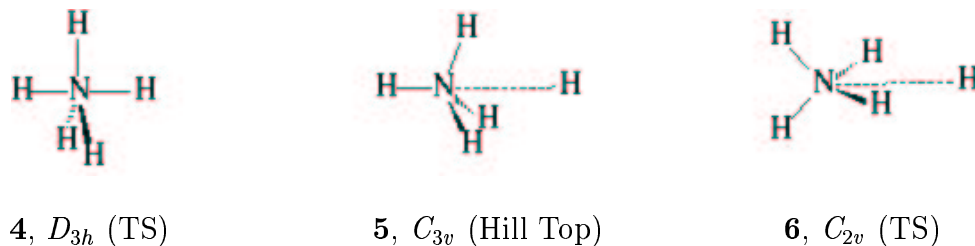
Ab initio CCSD(full)/6-311++G(3df,2p) calculations were performed for the bimolecular complex $\text{NH}_3 \cdots \text{H}_2$ and its rearrangements. The *ab initio* calculations performed predict the existence of sufficiently stable bimolecular complexes $\text{NH}_3 \cdots \text{H}_2$ with the very small complexation energy of about 0.02 kcal/mol. A peculiar topology of the PES is found around a saddle point of index two.

1. Introduction

Intermolecular interactions play a crucial role in defining the molecular structure of compounds with spatially suitably fitted functionalities, secondary and tertiary structures of biologically important macromolecules and modes of packing molecules in crystal, i.e. solid-state structures as well. The most important type of intermolecular interaction involves hydrogen and main group element donating electrons from lone-pairs or π -orbitals which relate to one of the donor-acceptor type intermolecular interactions [1-7]. During the last two decades various gas phase donor-acceptor complexes have become a topic of rapidly growing interest [4-7]. Theoretical and experimental studies of different gas phase van-der-Waals, electrostatic and donor-acceptor complexes permit to gain an insight into the origin of the specific attractive forces within the electron-abundant and electron rich centers in molecules. The present work is aimed at elucidating this interaction between H_2 and NH_3 in the gas phase with the help of *ab initio* calculations of the weak complexes **1** and **2** and ammonia inversion $1 \rightleftharpoons 3 \rightleftharpoons 2$ in this complex. Apart from the structural information relevant to the intermolecular



donor-acceptor interaction $H_2 \cdots NH_3$, particular attention has been given to the potential energy surface (PES) topology of the NH_5 system in the region of structures **4-6** correspondingly, and its unusual rearrangement pathways. Up to now, despite many



controversial examples [8-14], the reaction path has been considered to be a smooth continuous line connecting the saddle point (SP) with both minima corresponding to

reagent and product [15]. Early it has been shown that the steepest descent line or gradient line can connect one SP to another SP [8,9,12] in case of symmetry. The reaction path may consist of several different gradient lines connected over a corner at an SP [9]. In the present work we give the first example of how the reaction path (steepest descent line) emanating from saddle point **4** along the transition vector enters the neighboring stationary point **5** of index two ($\lambda=2$, hereafter, λ designates the number of the negative eigenvalues of the Hessian, cf. [16]).

2. Methods

All calculations of the stationary point optimization in this work were performed by standard CCSD(full)/6-311++G(3df,2p) methods using the Gaussian-98 [17] packages of *ab initio* programs. The optimization of the molecular geometry at stationary points at all levels of approximation was carried out with the "tight" convergence criterion. No counterpoise corrections were made for the basis set superposition error (BSSE) [18] in calculations concerned with the complex **1** because BSSE is a non-physical effect and there is a continuous discussion of its accounting [19-23]. Furthermore, it was found [23] that inclusion of BSSE often enormously decreases the thermodynamic stability and binding energy in various multimolecular complexes. (For example, the calculations of the alanine dimer give rise to the interaction energy of -19.7 kcal/mol, while including the BSSE affords the value of +14.4 kcal/mol [23].) All results obtained relate to the gas phase.

Splitting of the vibration levels for **1** and ammonia is calculated in the one-dimensional approximation of the adiabatic inversion potential by solving the Schrödinger equation with Hamiltonian

$$\mathbf{H} = -\frac{1}{2} \frac{d^2}{ds^2} + V(s) ,$$

where $V(s)$ is the adiabatic potential of the umbrella mode, and s is the step length of the IRC [10] in a.u.

3. Results and discussion

Stationary points on the $\text{H}_2 \cdots \text{NH}_3$ PES

According to our *ab initio* calculations performed at least six stationary points exist on the $\text{H}_2 \cdots \text{NH}_3$ PES, which correspond to structures **1-6**. We do not consider different structures that correspond to radicals or results of ammonia dissociation. Structures **1** and **2** correspond to minima ($\lambda=0$), structures **3**, **4** and **6** relate to saddle points ($\lambda=1$), and structure **5** corresponds to a "two dimensional hill" ($\lambda=2$). The values of the total and relative energies, and the zero point energies (ZPE) of structures **1-6**, and of the ammonia and the hydrogen molecules are listed in Table 1. The optimized geometries of the isomers **1-6**, of NH_3 and H_2 are featured in Figures 1, 2. It is worth noting that the results obtained for NH_3 and H_2 are in good agreement with experimental data [24]. The dipole complex **1** is predicted to have C_{3v} symmetry with the N...H distance slightly elongated compared to the sum of the van-der-Waals radii (2.66 \AA) [25] and shorter than the intermolecular distance in the complex $\text{H}_2\text{-N}_2$ (3.40 \AA) [26]. The complexation energy of **1** is very small, -0.024 kcal/mol , whereas for the second complex **2** this energy is positive, 0.497 kcal/mol . That shows that **2** is unstable relative to a dissociation into the fragments NH_3+H_2 . To the authors knowledge no experimental data on the type **1** bimolecular complex are currently available, and the complexation energy calculated can only be compared with experimental ($0.0692 \pm 0.0035 \text{ kcal/mol}$) and theoretical (0.103 kcal/mol) data for the stabilization energy of the $\text{H}_2\text{-H}_2$ complex [26]. Account that the ZPE totally changes the complexation energies for **1** (0.611 kcal/mol) and **2** (0.418 kcal/mol), and that it makes both structures **1** and **2** unstable relative to dissociation into the fragments NH_3+H_2 . However it appears that the complex **1** can be fixed in a frozen hydrogen matrix at a low temperature. The bond lengths and values of angles in the NH_3 and H_2 fragments are nearly not changed in complexes **1** and **2** in comparison to those in isolated molecules.

Ammonia inversion

The ammonia inversion in the complex $\text{H}_2 \cdots \text{NH}_3$ occurs via transition state structure **3** corresponding to a true saddle point ($\lambda=1$) on the NH_5 PES with an energy barrier of 5.21 kcal/mol. This value is a little bit lower than the inversion barrier of 5.58 kcal/mol calculated for ammonia [24]. It is very interesting to ascertain splitting vibration levels in the one-dimensional approximation for complex **1**, in comparison with ammonia. This is shown in Figure 3 where the dashed curve gives the potential energy of ammonia. The solid curve is the potential of the complex $\mathbf{1} \rightleftharpoons \mathbf{2} \rightleftharpoons \mathbf{3}$. "Five" vibration levels in the double-well potential for ammonia (left) correspond "six" vibration levels of the complex $\mathbf{1} \rightleftharpoons \mathbf{2}$ (right). The calculated values and the experimental measurement [24] of the vibration levels in **1** and in ammonia are listed in Table 2. The splitting of the first two levels is quite larger for complex **1** than for ammonia whereas the remaining levels are not markedly different. For ammonia the first level splitting is in the microwave region [27], whereas in complex **1** it may be already searched for in the far infrared.

PES transformation along reaction path

The bipyramidal structure **4** of D_{3h} symmetry corresponds to a saddle point ($\lambda=1$) and is the true transition state for the S_N2 identity reaction at nitrogen. The reaction path (steepest descent) emanating from **4** along the transition vector enters the next stationary point with a $\lambda=2$ relating structure **5**. The point symmetry group C_{3v} is conserved along this reaction path. Two steepest descent paths emanating from **5** tangentially the two Hessian eigenvectors correspond to the negative degenerate eigenvalues (e-symmetry [27],p. 241). They enter saddle point **6** ($\lambda=1$) and minimum **1** ($\lambda=0$), respectively. The strange transition to an SP of index two from above may be explained more deeply with the help of Figure 4. It shows (on the 6-31G** level) the change of the modes which receive negative eigenvalues at one of the two SPs of interest. At structure **4**, the asymmetric stretch mode along the "grab handle" of the umbrella is the decay mode. A bend mode has a positive eigenvalue, but it is degenerate, it is two-fold. The steepest descent $\mathbf{4} \rightarrow \mathbf{5}$ is mainly the asymmetric stretching/shortening of the stick of the umbrella (connected with a small part of the umbrella mode). Somewhere

at the pathway **4-5**, the bend mode crosses a valley-ridge inflection point (VRI) [28], and then changes to a negative curvature. Some steps later, the former negative stretch mode along the reaction coordinate transforms into a positive mode. Finally, at SP **5** we find the two-fold degenerate bending being the decay mode. It concerns the bending orthogonal to the linear structure of the stick, thus a usual SP of index two [16]. A schematic view of the pathway in a section of the two-dimensional bending mode is shown in Figure 5. The reaction path is again the steepest descent **4**→**5** which changes the distances of the stick of umbrella **4**. Such an unusual topology of the PES is obtained for the first time and leads to the two following important conclusions.

- First, there is no any limitation of the distribution of various types of stationary points on the PES. An early similar limitation is considered to be the Morse relations. However, the Morse relations only can be applied to the distribution of non-degenerate stationary points in a limited region of the PES of full $3N-6$ dimensions. Thus, the necessity to remove all degenerate stationary points and poles from consideration makes the application of the Morse relations non-effective in practical use.
- Second, it is impossible to introduce strong rules for symmetry elements (or the symmetry point group) conserving from one minimum (reagent) via transition state structure to another minimum (product). The usual symmetry conservation rules are based on the presumption that the reaction path which connects two minima (reagent and product) via an SP (transition state structure) is the single continuous steepest descent line not trespassing other stationary points. Indeed in this case, according to Pearson's theorem [29], the symmetry elements are conserved along the reaction path; they contain symmetry elements of both reagent and product. Or, the symmetry point group which is conserved along the reaction path is a subgroup of the symmetry point groups of reagent, transition state structure and product. However, here appears another stationary point with $\lambda > 1$, where the reaction path changes its direction, on the steepest descent path from the higher transition state.

4. Conclusions

The *ab initio* calculations carried out show that there exists a weak intermolecular dipole interaction that stabilizes the linear C_{3v} -configuration of the complex $\text{NH}_3 \cdots \text{H}_2$. An unusual topology of the reaction paths is obtained by a pathway from an SP of index one downhill to an SP of index two. The relation of the two SPs is enlightened.

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Table I. *Ab initio* CCD(full)/6-311++G(3df,2p) data for the structures **1-6**, NH₃ and H₂.^a

Structure, symmetry	E _{tot}	ZPE	λ	ΔE	ΔE _{ZPE}	ΔH	ΔG	ω ₁ / iω ₁
1, C _{3v}	-57.656879	0.047035	0	0.0	0.0	0.0	0.0	62(e)
2, C _{3v}	-57.656048	0.045896	0	0.52	-0.19	0.33	-1.86	37(e)
3, C _{3v}	-57.648571	0.045240	1	5.21	4.09	4.22	3.72	i839
4, D _{3h}	-57.471557	0.046704	1	116.29	116.08	114.31	119.46	i1253
5, C _{3v}	-57.543056	0.050487	2	71.42	73.59	71.68	76.57	i465(e)
6, C _{2v}	-57.546647	0.049632	1	69.17	70.80	69.28	73.15	i936
NH ₃ , C _{3v}	-56.486124	0.034943	0	0.0	0.0	0.0	0.0	1055
NH ₃ , D _{3h}	-56.477224	0.033524	1	5.58	4.07	4.05	4.52	i840
H ₂ , D _{∞h}	-1.1707166	0.010080	0	-	-	-	-	4425

^a) E_{tot} (in a.u.) - total energy (1 a.u.=627.5095 kcal·mol⁻¹),

ZPE (in a.u.) - harmonic zero-point correction,

λ - the number of the negative Hessian eigenvalues,

ω₁ or iω₁ (in cm⁻¹) - the smallest or imaginary harmonic vibration frequency,

ΔE (in kcal·mol⁻¹) - relative energy (1 a.u.=627.5095 kcal·mol⁻¹),

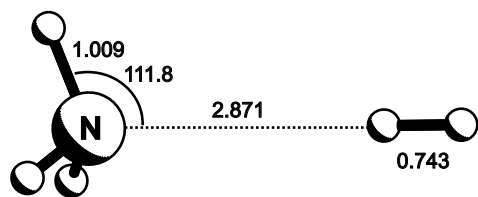
ΔE_{ZPE} (in kcal·mol⁻¹) - relative energy including harmonic zero-point correction,

ΔH and ΔG (in kcal·mol⁻¹) - relative enthalpy and Gibbs free energy at standard conditions $P=1$ ATM and $T=298.1$ K.

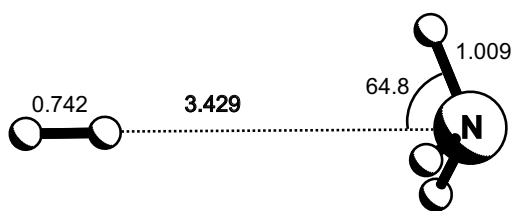
Table II. Vibrational frequencies for $\text{NH}_3 \cdots \text{H}_2$ and NH_3 (cm^{-1}).^a

n	$\text{NH}_3 \cdots \text{H}_2$	NH_3	NH_3
	This work	This work	Exp.[24]
0	0.0	0.0	0.0
1	202.91	1.02	0.79
2	907.24	903.67	932.43
3	1089.09	938.59	968.12
4	1638.25	1568.48	1598.47
5	1898.23	1825.47	1882.18
6	2364.02	2313.31	2384.17
7	2819.79	2785.81	2895.61

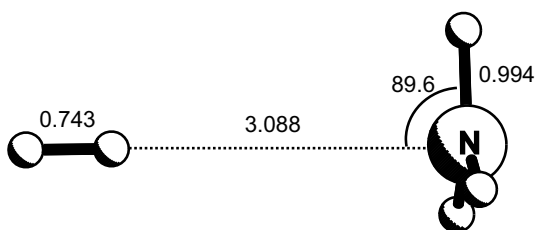
^a) n – quantum number equal to number of wave function nodes.



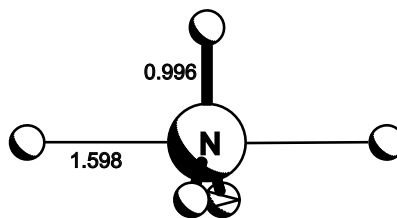
1, $C_{3v} (\lambda=0)$



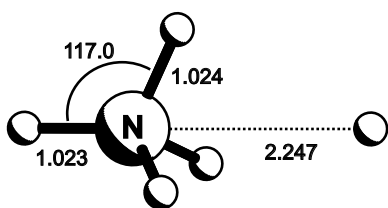
2, $C_{3v} (\lambda=0)$



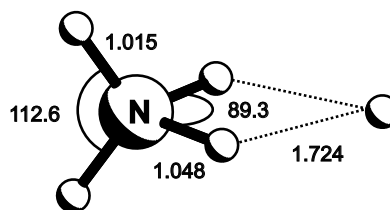
3, $C_{3v} (\lambda=1)$



4, $D_{3h} (\lambda=1)$



5, $C_{3v} (\lambda=2)$



6, $C_{2v} (\lambda=1)$

FIG. 1 Minyaev et al.

Geometrical parameters for structures 1-6, as predicted by *ab initio* methods. Bond lengths and valence angles are given in Å and degrees, respectively.

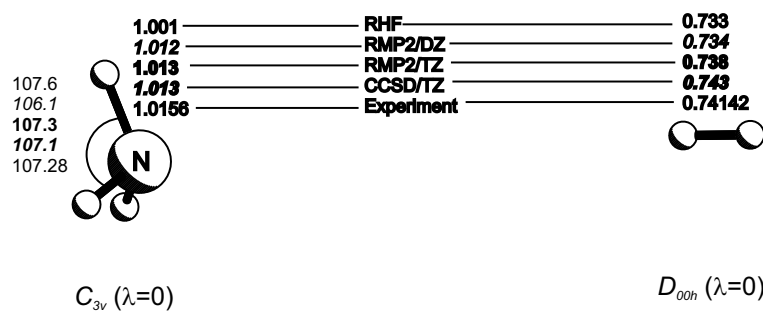


FIG. 2 Minyaev et al.

Geometrical parameters for structures of ammonia and H_2 , as predicted by *ab initio* methods. Bond lengths and valence angles are given in Å and degrees, respectively.

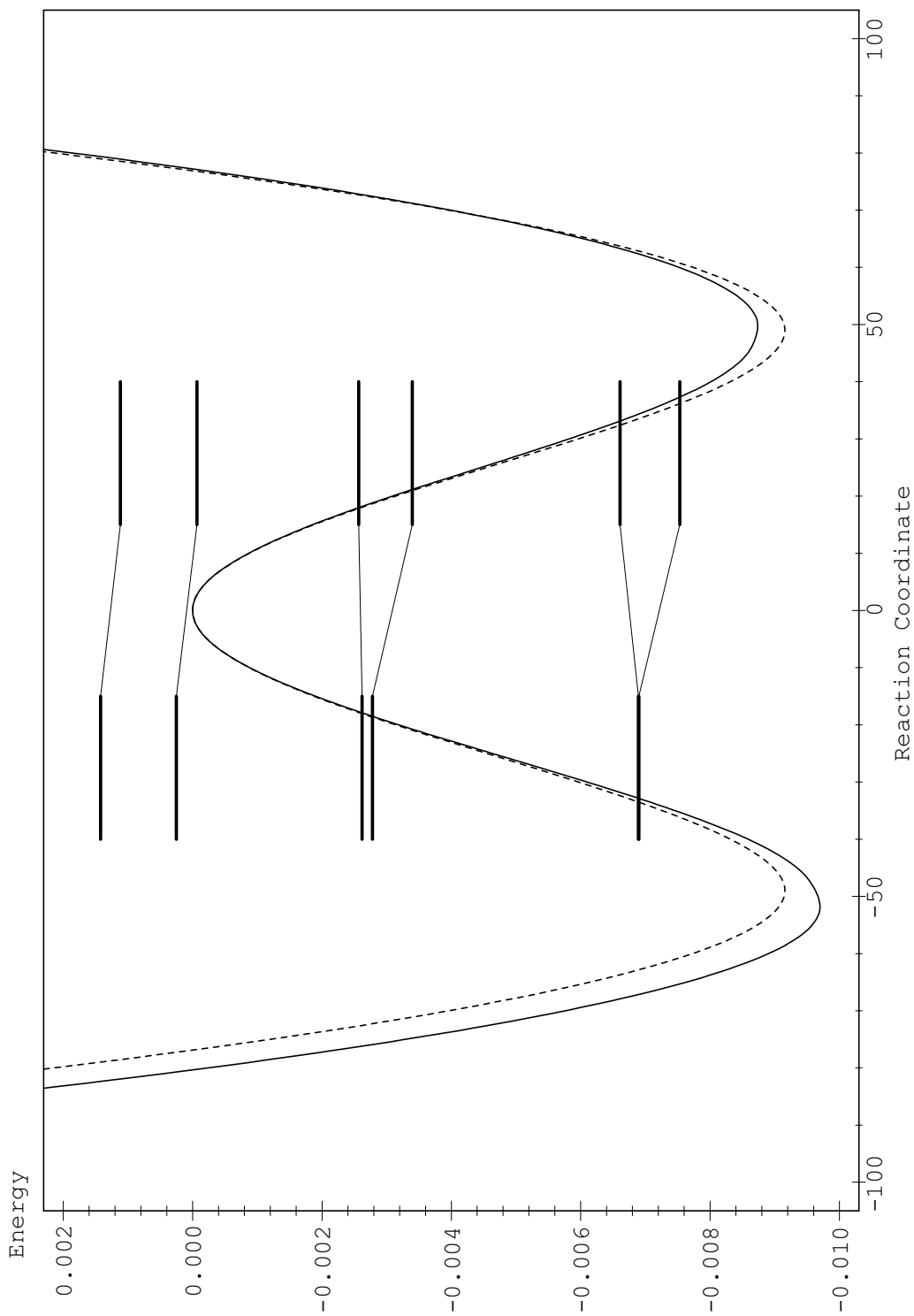


FIG. 3 Minyaev et al.

Tunneling splitting in the ammonia inversion potential in pure NH₃, and in the complex NH₃...H₂. The potential energy is given in a.u., the energy of ammonia is the dashed curve.

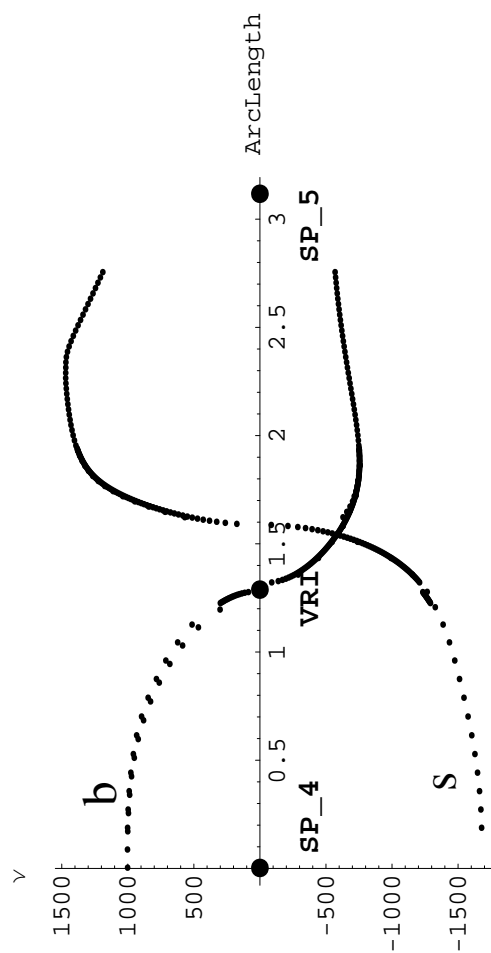


FIG. 4 Minyaev et al.

Two decay modes, **s** for stretch and **b** for bend, of structures **4**, **5** along the steepest descent from **4** to **5** over the arclength scale of the IRC calculation.

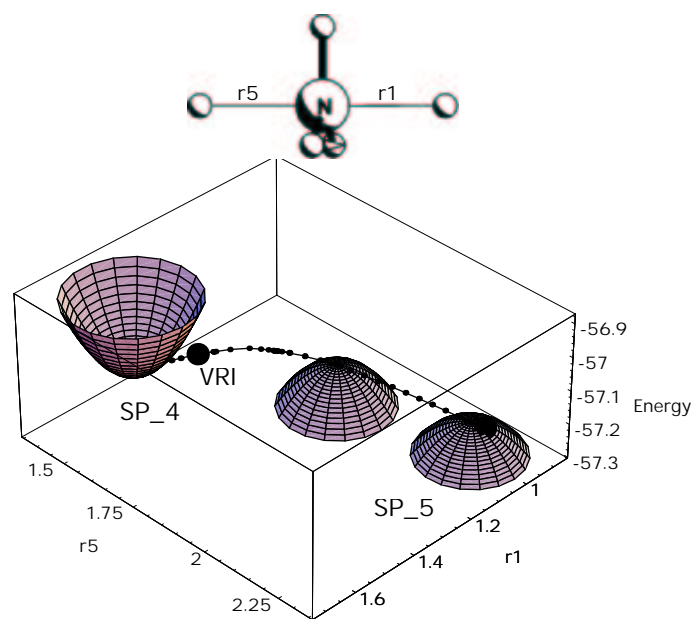


FIG. 5 Minyaev et al.

Schematic view of the two-fold potential of the bending mode along the steepest descent from **4** to **5** seen over the coordinate plane of r_1 , r_5 .