



Molecular Dynamic Investigation of HN₂ On A Potential Energy Surface Designed By Lie Algebra Method

Hassan Talaat¹, Ali H. Moussa¹, M. Shalaby¹, El-Wallid S. Sedik^{2*}

¹Physics Dept., Faculty of Science, Ain Shams University, Cairo, Egypt

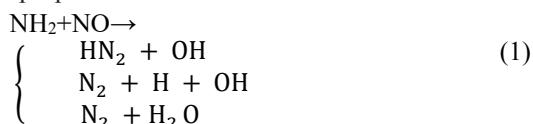
²Theoretical Physics Dept., National Research Center, Dokki, Giza, Egypt

WE have used Algebraic method especially Lie algebra to generate the contour plot of HN₂ potential energy surface then we performed detailed dynamic calculations on Lie algebra potential surfaces (LPES) representing the ground electronic potentials of the collinear HN₂ reaction. The Lie Surface generated produce accurate results for the life time. The structure was found to be metastable. The novel reaction dynamics are examined in detail.

Keywords: Lie algebra, Potential energy surface, Molecular dynamics.

Introduction

Many experimental and theoretical studies have attempted to elucidate the possible role of the HN₂ species as a critical step in various reactions. Although this molecule has never been observed experimentally, it has been postulated to be an important intermediary in thermal processes, [1,2] with indirect evidence that suggests its existence through the three possible product channels proposed for the NH₂ + NO reaction:



The experiments that are focused to determine the rate coefficient and the major pathway of reaction 1 are far from consistent: although the experimental studies vary widely, in regard to the branching ratio for OH production, none of the experiments observed H atoms [3]. This result, along with the assumed product channels, argues for the existence of the HN₂ species. However, a controversy persists from the kinetics modeling studies [2,4]. In fact, although an estimate of 10⁻⁴ s for the lifetime produces a reasonable match to experimental observations, the theoretical studies of HN₂ unimolecular decay predict a much shorter value, of 10⁻⁸-10⁻⁹ s, for the ground vibrational state [5-7].

Many ab initio studies of the reaction have previously been made to characterize the geometry and energetics of the reactants, transition state, and products [3]. All previous calculations concluded that the title system is quasibound (the global minimum is located above the H + N₂ asymptote) with a barrier height to dissociation of ~11 kcal/mol. From such studies, a global potential energy surface was reported by Walch [5,8,9] and Koizumi et al. [6] for the H + N₂ channel. On the basis of a spline fit of the ab initio points calculated using the completed active space self-consistent field/ externally contracted configuration interaction (CASSCF/CCI) method and two different basis sets, Walch and co-worker predicted, depending on the basis set used, a barrier height of 10.2 or 11.3 kcal/mol and a global minimum of 5.6 or 3.9 kcal/mol above the H + N₂ asymptote.

Walch and Partidge [10] attempted a conclusive and accurate prediction of the HN₂ unimolecular decomposition. They reported a systematic study of the HN₂ energetics which yields a barrier height of 11.34 kcal/mol and a global minimum 4.31 kcal/mol above the H + N₂ asymptote. A slight difference between the constrained minimum reaction path calculated at this level of theory and the one previously estimated using a potential energy surface [6]. Gu et al. [13] predict the

*Corresponding author: *e-mail: elwallids@gmail.com

DOI : 10.21608/ejphysics.2021.60392.1063

Received : 29/1/2021; accepted : 14/6/2021

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classical barrier height for the reaction $\text{HN}_2 \rightarrow \text{H} + \text{N}_2$ to be 10.7 kcal/mol, thus lying 0.6 kcal/mol below the extrapolated value reported by Walch and Partridge [10]. In turn, the calculated [13] exothermicity for the reaction $\text{H} + \text{N}_2 \rightarrow \text{HN}_2$ is 3.8 kcal/mol, which is, thus, slightly smaller than the extrapolated value [10] of 4.31 kcal/mol. We may therefore argue that there is not a conclusive result yet for the HN_2 lifetime.

In this work, we report the potential energy surface for the ground electronic state of the title system, based on Algebraic approach. The Lie Algebra method has been extensively used in chemical physics and molecular physics after Iachello and Levine treated the molecular vibrational problems using Lie algebraic approach [14,15]. The potential energy surfaces of linear triatomic molecules was obtained [16] using $U(4)$ algebra by introducing a transformation between the angle of canonical coordinates and the bond angle. This potential energy surface can be used to describe the stretching motion of two bonds and the bending motions of the bond angle. We shall also show how to implement the method in the dynamics of the reaction on Lie constructed potential energy surface LPES in the case of linear molecules. We have chosen the HN_2 molecule.

The paper is organized as follows. In section 2 briefly reviews that the algebraic approach applied to potential energy surfaces are given. Theory is presented in section 3. In section 4 the dynamics of HN_2 molecule on the constructed Lie potential surface are obtained. Conclusion are presented in section 5.

Potential energy surface

It is suitable to describe triatomic molecules using $U(4)$ algebra. In this case triatomic molecules are of dynamical symmetric chain.

$$U_1(4) \otimes U_2(4) \supset \left\{ \begin{array}{c} O_1(4) \otimes O_2(4) \\ U_{12}(4) \end{array} \right\} \supset O_{12}(4). \quad (1)$$

Here, $O_{12}(3)$ and $O_{12}(2)$ are throw out since the rotation of triatomic molecules is not considered.

The Hamiltonian of triatomic molecules for the chain (1) is

$$H = A_1 C_1 + A_2 C_2 + A_{12} M_{12} + \lambda M_{12}, \quad (2)$$

where A_1 , A_2 , A_{12} , M_{12} , and λ are expansion coefficients, and they can be determined by fitting spectroscopic data. C_1 and C_2 are the Casimir operators of $O_1(4)$ and $O_2(4)$, respectively. and

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are the two Casimir operators of $O_{12}(4)$, M_{12} is so-called Majorana operator, and it relates to the Casimir operator of $U_{12}(4)$.

It is obvious that the algebraic Hamiltonian (2) has no directly single geometrical meaning, but one can extract potential functions from this algebraic Hamiltonian [16,17]. We can apply above equations to the determination of the PES of the linear molecular HN_2 .

The expansion coefficients in equation (2) can be obtained by fitting spectroscopic data.

The Potential Surface can be written as follows:

$$\begin{aligned} V_{LiePES}(q_1, q_2, \phi) = & (A_1 + A_{12}) N_1^2 [2 - e^{-\beta_1(q_1 - q_{1c})}] e^{-\beta_1(q_1 - q_{1c})} \\ & + (A_2 + A_{12}) N_2^2 [2 - e^{-\beta_2(q_2 - q_{2c})}] e^{-\beta_2(q_2 - q_{2c})} \\ & + 2A_{12} N_1 N_2 \{ [2 - e^{-\beta_1(q_1 - q_{1c})}] e^{-\beta_1(q_1 - q_{1c})} \\ & \times [2 - e^{-\beta_2(q_2 - q_{2c})}] e^{-\beta_2(q_2 - q_{2c})} \}^{1/2} \cos \alpha(\phi - \pi) \\ & + \frac{1}{4} \lambda N_1 N_2 \{ (2e^{-\beta_1(q_1 - q_{1c})} + 2e^{-\beta_2(q_2 - q_{2c})} \\ & - 2e^{-\beta_1(q_1 - q_{1c}) - \beta_2(q_2 - q_{2c})}) \cos \alpha(\phi - \pi) \\ & - 2[(2 - e^{-\beta_1(q_1 - q_{1c})}) e^{-\beta_1(q_1 - q_{1c})} (2 - e^{-\beta_2(q_2 - q_{2c})} \\ & \times e^{-\beta_2(q_2 - q_{2c})})]^{1/2} \cos \alpha(\phi - \pi) \}, \end{aligned}$$

$$\text{where } \alpha = |\alpha| \quad (3)$$

The Lie potential energy surface, V_{Lie} for HN_2 molecule in which the bond angle is frozen at equilibrium position. Contours drawn at intervals of $0.009 E_h$, starting at $-0.1335 E_h$ and three-dimensional Lie Potential energy surface for the motion of the oxygen atom around the NN fragment. a) in bond distance, b) in Skewed coordinates as shown in Fig.1.

Theory

The time-dependent Schrödinger equation in which the quantum dynamical behavior of our model system is contained and which can be expressed shortly as:

$$i \hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi(q_1, q_2, t) \quad (4)$$

By introducing the skewed coordinates q_1, q_2 it becomes:

$$H = -\frac{\hbar^2}{2\mu} \left[\frac{\partial^2}{\partial q_1^2} + \frac{\partial^2}{\partial q_2^2} \right] + V_{LiePES}(q_1, q_2) \quad (5)$$

a)

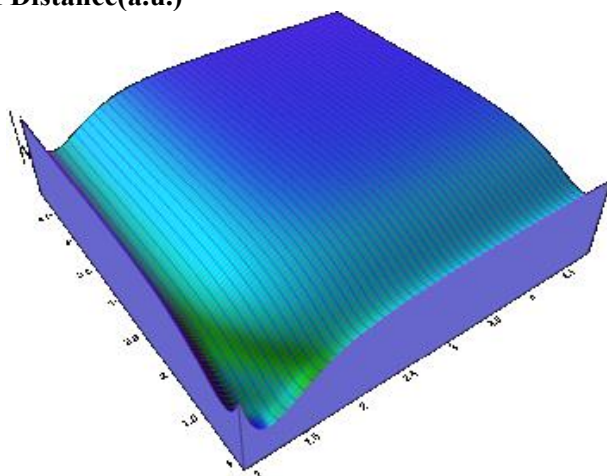
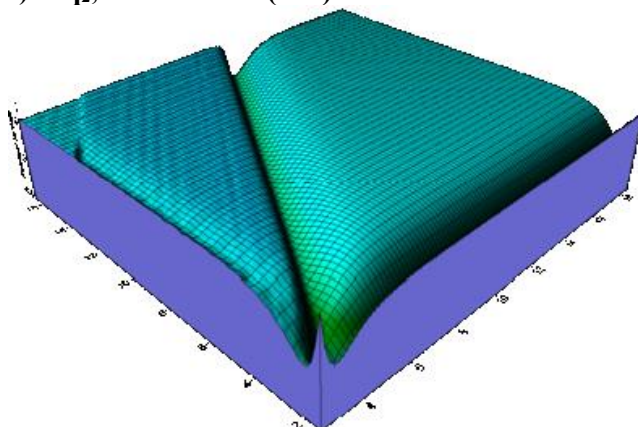
 $r_2, \text{N-H Distance (a.u.)}$  $r_1, \text{N-H Distance (a.u.)}$ b) $q_2, \text{N-H Distance (a.u.)}$  $q_1, \text{N-H Distance (a.u.)}$

Fig. 1. Isoenergy contour plot for the stretching of the two NH bonds in linear N-H-N. Contours are equally spaced by $0.009 E_h$, starting at $-0.1335 E_h$. The two equivalent structures $\text{NH}\dots\text{N}$ and $\text{N}\dots\text{HN}$ indicate linear transition states, which appear as hydrogenbonded minima, with respect to the stretching coordinate. b) in Skewed coordinates.

where

$$\mu = \left[\frac{m_1 m_2 m_3}{m_1 + m_2 + m_3} \right]^{1/2}$$

be formally integrated to give:

$$\Psi(q_1, q_2, \Delta t) = U(\Delta t) \Psi(q_1, q_2, 0), \quad (6)$$

where $U(\Delta t) = \exp[-(i \Delta t / \hbar) H]$ is the time evolution operator. In order to advance the wave function through n time steps, we repeatedly apply $U(\Delta t)$ starting with the initial wave function using high order finite difference algorithms [18]. After n steps, we have

$$\Psi(q_1, q_2, n\Delta t) = U^n(\Delta t) \Psi(q_1, q_2, 0), \quad (7)$$

The wave function is specified at time $t = 0$ and propagated to later times. A wave-packet is needed to represent the initial state of the system. Far from the interaction region of the (PES), there is no interaction.

For HN_2 calculations the time interval is $\Delta t = 0.045$ Femtosecond $= 0.045 \times 10^{-15}$ sec., and mesh spacing are $\Delta q_1 = \Delta q_2 = 0.05$ a.u. - the mesh normally contains $\sim 10^6$ points. The center of the initial wave-packet is placed at $= 27.5$ a.u. in the reactant region. For the width parameter d in the Gaussian function we applied the value 0.25 a.u.. All calculations are carried out for reactant molecules in their ground states for collinear configurations of the three interacting species and for one translational energy value of the initial Gaussian wave-packet, namely, 11.5 kcal/mol.

Dynamical calculation

The barrier height for the process $\text{HN}_2 \rightarrow \text{H} + \text{N}_2$ is predicted to be 10.6 kcal/mol before inclusion of the zero-point energy correction. Thus, it lies slightly below the 11.3 kcal/mol extrapolation of Walch and Partridge,[10] while being very similar to the result reported by Gu et al. [13] These authors having predicted a barrier height of 10.7 kcal/mol. the literature shows that the estimated values for the barrier height have a tendency to show a

more stable value 11 kcal/mol than the calculated exothermicity for the reaction $\text{HN}_2 \rightarrow \text{H} + \text{N}_2$.

The scattering calculations were restricted to collinear geometries with a linear transition state, which suggests that collinear geometries may dominate the reaction. A LPES potential energy surface was used; the present study reports the results of the quantum mechanical wave-packet approach of the HN_2 (LPES). We visualize the wave packet propagation at fixed times – to gain insight into the nature of the reaction process. Figures 2.a,b,c,d,e,f,g and h show such snapshots. The region being viewed contains the reactant, the interaction and the product regions.

After 1000 time steps the center of the wave is found at $q_1 = 10.0$ a.u. as shown in Fig. (2.b). The wave packet has also clearly broadened. In Figure (2.c) (time-step 3000) the wave packet is just entering the interaction region and has more than one peak. At time step 3800 (Fig. (2.d)) there are

drastic alterations in the form of the wave-packet which shows multiple interference maxima [19]. The largest maxima are on the left.

At time steps $3900\Delta t$, $4000\Delta t$, (Figs. 2.e and 2.f) show the packet spreading and entering the interaction region. At time steps 5000 , 6000 , 7000 (Figs. 2.g, 2.h) show the production of ripple maxima throughout the part of the wave-packet that reflects back into the reactant region, because of the very short life time [20-22] part of the wave packet is trapped and the major part dissociates ignoring laser effect [23]. The dissociation is fast.

The time threshold of the reaction for the calculations (Fig. 3) with the Lie (PSs) ranges from 3000 to 5000 time steps, the higher the collision energy the lower is the time threshold. The reaction probability increases smoothly in the time step range 3000 - 6000 . Thereafter, it increases slowly until about 5800 time steps, where it becomes nearly constant. For collision energy $E = 11.5$ kcal/mol the reaction probability is 0.46 .

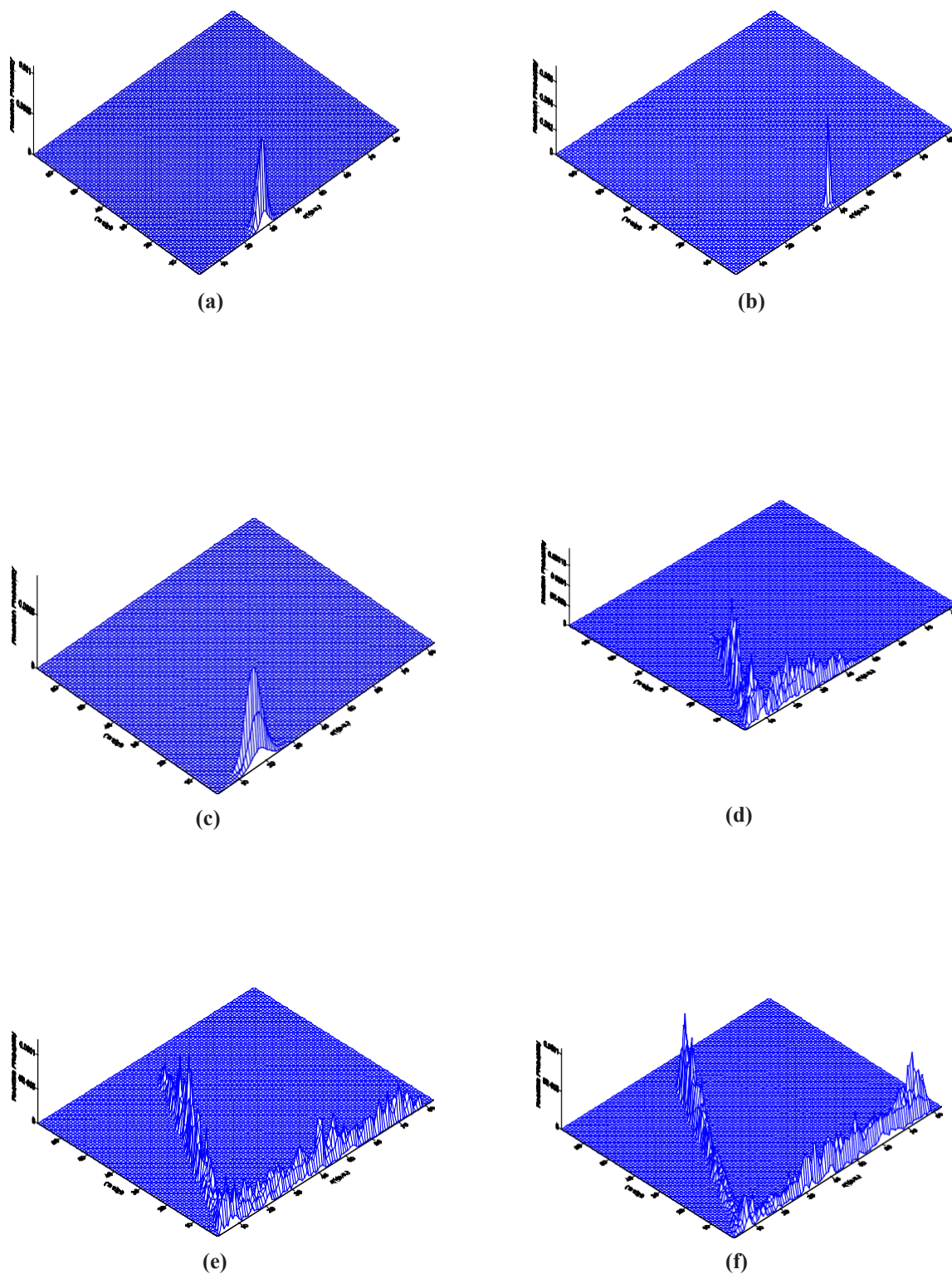


Fig. 2. “ Snapshots ” of the reaction probability for the collinear HN_2 reaction on the Lie (PES) for the case $v = 0$, $E_{\text{trans.}} = 11.5$ kcal/mol. (One time step $\Delta t = 0.045$ Femtosecond.).

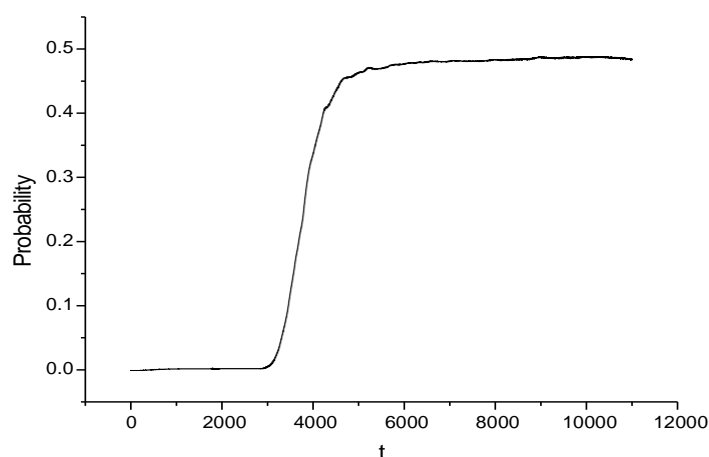


Fig. 3. Plot of the reaction probability versus time for the collinear HN_2 reaction on the Lie (PES) for the case $\mathbf{v} = \mathbf{0}$, $E_{\text{trans.}} = 11.5$ kcal/mol. (One time step $\Delta t = 0.045$ Femtosecond.).

Conclusion

We have reported a dynamical calculation on Lie potential energy surface for ground-state HN_2 . The various topographical features of the new potential energy surface have been carefully examined and compared with previous calculations for the title system, most importantly, a potential energy surface that was previously reported by Walch and collaborators [5,6,8,9]. The geometries and spectroscopy of the main stationary points for the HN_2 global minimum, transition state for dissociation, barrier height are reproduced very accurately when compared with the best available theoretical estimates. We emphasize that the predicted barrier height for dissociation lies below the best available estimates, [10,13] which suggests a rigid ground to perform dynamic calculation. Thus, we speculate that dynamics calculations that we used on the Lie potential energy surface are likely to predict a lifetime of 10^{-11} s for the HN_2 species that is even shorter than previously reported estimates. The stability of the structure is found to be a metastable one. The reaction probability was found to be 0.46. To summarize, the Lie potential energy surface reported in the present work is being recommended for further future dynamics studies of the $\text{H} + \text{N}_2 \rightarrow \text{HN}_2 \rightarrow \text{HN} + \text{N}$ reaction.

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