N_2O Dissociation Mechanism Using Algebraic Methods

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We apply the time-dependent theory to the collinear reaction N_2O. We have performed detailed calculations on Lie algebra potential energy (LPE) representing the potentials of the collinear N_2O reaction. The Lie potential has a transformation between the angle of canonical coordinates and the bond angle to describe the bending motion in the potential energy of bent triatomic molecules. Results for the linear triatomic molecule N_2O are reported.

1. Introduction

The nitrous oxide molecule has been an important subject of study in a number of scientific fields such as life sciences [1], earth sciences [2], atmospheric sciences [3], and fuel industry [4]. It has also been the subject of different theoretical and experimental studies [5−7].

It is a climatically important species affecting the Earth's radiation. Its contribution to the greenhouse effect is considerable due to its long residence time of 120± 30 years [8] and its relatively large energy absorption capacity per molecule [9]. On a per molecule basis, N_2O is estimated to be 296 times more powerful than CO_2 as a greenhouse gas (based on 100 year global warming potentials) [10]. Nitrous oxide is inert in the troposphere. However, in the stratosphere, especially in the middle and upper stratosphere, N_2O is destroyed by photolysis ($\lambda \sim 180\text{-}215$ nm):

$$N_2O + h\nu \rightarrow N_2 + O(^1D_2) \qquad (A)$$

Process A accounts for ~90% of photochemical N_2O destruction [8] The other 10% of N_2O photochemical loss is via reaction with $O(^1D_2)$[11]:

$$N_2 + O(^1D_2) \rightarrow N_2 + O_2 \qquad (B)$$
$$\rightarrow NO + NO \qquad (C)$$

About 40% of the $N_2 + O(^1D_2)$ reaction proceeds via channel B and about 60% via channel C. Reaction C represents the dominant source of total reactive nitrogen (NO_2) in the stratosphere [12,13].

Algebraic approach 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 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 can be used to describe the stretching motion of two bonds and the bending motions of the bond angle.

In this paper it shows how to implement the method in the dissociation of the reaction on Lie constructed potential energy LPE in the case of linear molecules. We have chosen as an example the N_2O molecule.

The paper is organized as follows. In section 2 briefly reviews that the algebraic approach applied to potential energy are given. Theory is presented in section 3. In section 4 the dissociation of N_2O molecule on the constructed Lie potential energy are obtained.

2. Lie Potential Energy

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

$$U_1(4) \otimes U_2(4) \supset \begin{Bmatrix} O_1(4) \otimes O_2(4) \\ U_{12}(4) \end{Bmatrix} \supset O_{12}(4). \qquad (1)$$

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

$$H = A_1 C_1 + A_2 C_2 + A_{12} C_{12}^1 + A_{12}' C_{12}^2 + \lambda M_{12}, \qquad (2)$$

where A_1, A_2, A_{12}, A_{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. C_{12}^1 and C_{12}^2 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 PE of the linear molecular N_2O.

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

The Lie Potential energy can be written as follows:

$$
\begin{aligned}
V_{LiePE}(q_1, q_2, \phi) &= (A_1 + A_{12})N_1^2[2 - e^{-\beta_1(q_1 - q_{1e})}]e^{-\beta_1(q_1 - q_{1e})} \\
&+ (A_2 + A_{12})N_2^2[2 - e^{-\beta_2(q_2 - q_{2e})}]e^{-\beta_2(q_2 - q_{2e})} \\
&+ 2A_{12}N_1N_2 \Big\{ [2 - e^{-\beta_1(q_1 - q_{1e})}]e^{-\beta_1(q_1 - q_{1e})} \\
&\times [2 - e^{-\beta_2(q_2 - q_{2e})}]e^{-\beta_2(q_2 - q_{2e})} \Big\}^{\frac{1}{2}} \square \cos\tilde{\alpha}(\phi - \pi) \\
&+ \frac{1}{4}\lambda N_1 N_2 \Big\{ (2e^{-\beta_1(q_1 - q_{1e})} + 2e^{-\beta_2(q_2 - q_{2e})} \\
&- 2e^{-\beta_1(q_1 - q_{1e}) - \beta_2(q_2 - q_{2e})} \square \cos\tilde{\alpha}(\phi - \pi) \\
&- 2[(2 - e^{-\beta_1(q_1 - q_{1e})})e^{-\beta_1(q_1 - q_{1e})}(2 - e^{-\beta_2(q_2 - q_{2e})} \\
&\times e^{-\beta_2(q_2 - q_{2e})}]^{1/2} \square \cos\tilde{\alpha}(\phi - \pi) \Big\},
\end{aligned}
\qquad \textbf{(3)}
$$

$$ where \quad \tilde{\alpha} = |\alpha| $$

The Lie potential energy, V_{Lie} for N_2O molecule in which the bond angle is frozen at equilibrium position. The Lie Potential energy for the motion of the oxygen atom around the NN fragment. a) in bond distance, b) in natural coordinates as shown in Fig.(1).
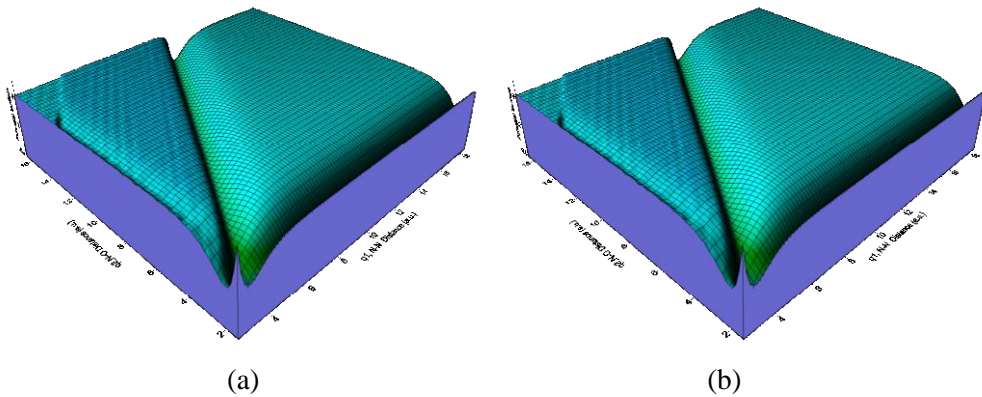

(a)   (b)

Fig.(1): Plot of the Lie potential energy, V_{Lie} for N_2O molecule, bond angle is frozen at equilibrium position for the motion of the oxygen atom around the NN fragment. a) in bond distance, b) in natural coordinates.

3. 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:

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

By introducing the natural coordinates q_1, q_2 it becomes:

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

where

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

be formally integrated to give:

$$\Psi(q_1, q_2, \Delta t) = U(\Delta t)\, \Psi(q_1, q_2, 0), \tag{6}$$

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

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

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 Potential energy, there is no interaction.

For N_2O calculations the time interval is $\Delta t = 0.045$ Femtosecond $= 0.045 \times 10^{-15}$ sec., and mesh spacing are $\Delta q_1 = \Delta q_2 = 0.02$ a.u. - the mesh normally contains $\sim 10^6$ points. The center of the initial wave-packet is placed at $q_1^o = 20.5$ a.u. in the reactant region. For the width parameter δ in the Gaussian function we applied the value 0.5 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, 1.7 eV.

4. Conclusions

The scattering calculations were restricted to collinear geometries with a linear transition state, which suggests that collinear geometries may dominate the reaction. A LPE potential energy was used; the present study reports the results of the quantum mechanical wave-packet approach of the N_2O (LPE). We visualize the wave packet propagation at fixed times – to gain insight into the nature of the reaction process. Fig. (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 $3500\Delta t$, $4000\Delta t$, (Figs. 2.e and 2.f) show the packet spreading and entering the interaction region. At time steps 50000, 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.
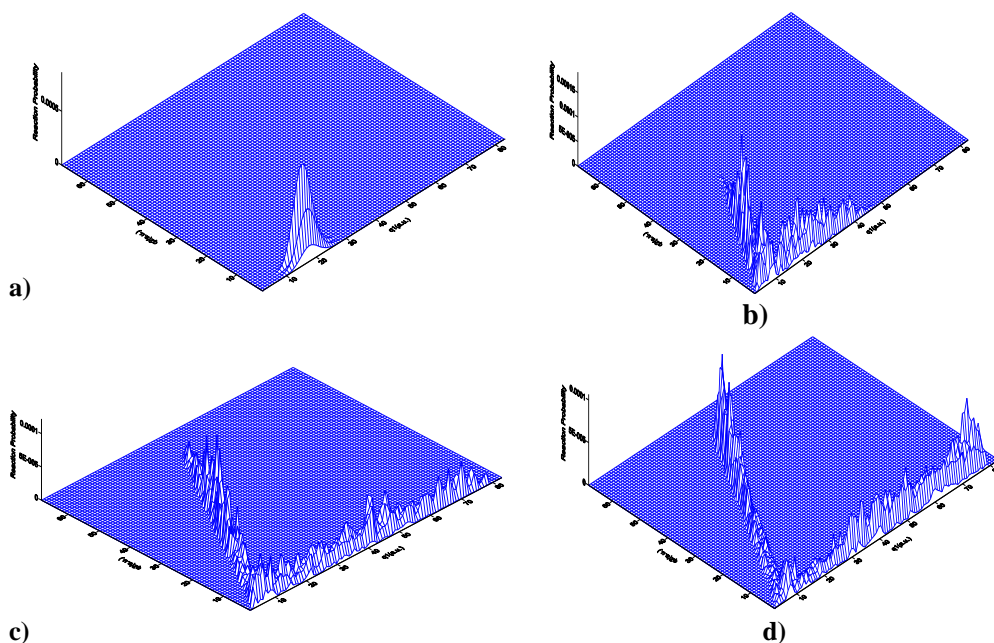

a)

b)

c)

d)

Fig.(2): Dissociation probability for the collinear N_2O reaction on the Lie potential energy for the case $\nu = 0$, $E_{trans.} = 1.7$ eV. (One time step $\Delta t = 0.025$ Femtosecond.).

The time threshold of the reaction for the calculations Fig.(3). with the Lie potential energy ranges from 2000 to 4000 time steps, the higher the collision energy the lower is the time threshold. The dissociation probability increases smoothly in the time step range 4000-5000. Thereafter, it increases slowly until about 5700 time steps, where it becomes nearly constant. For collision energy E = 1.7 eV the dissociation probability is 0.48.
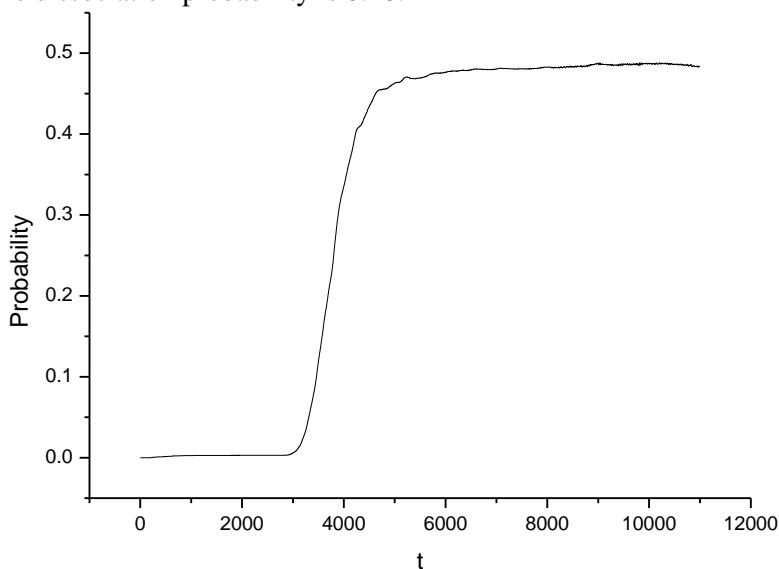

Fig.(3): Plot of the Dissociation probability versus time for the collinear N_2O reaction on the Lie potential energy for the case $\nu = 0$, $E_{trans.} = 1.7$ eV. (One time step $\Delta t = 0.025$ Femtosecond.).

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