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SO$_2$ Dissociation Mechanism Using Algebraic Methods

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WE apply the time-dependent theory to the reaction SO$_2$. We have performed detailed calculations on Lie algebra potential energy (LPE) representing the potentials of the SO$_2$ 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 triatomic molecule SO$_2$ are reported.

Keywords: Lie algebra, Potential energy, Dissociation.

Introduction

The elementary reactions involving the sulfur dioxide (SO$_2$) molecule have an important role in the combustion of sulfurcontaining materials [1]. In particular, the title reaction has been the subject of much experimental work [2-10], from which critical evaluations of the results have also been reported [11-13].

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 we show 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 SO$_2$ molecule.

The paper is organized as follows: section 2 briefly reviews the algebraic approach applied to potential energy. The theory is presented in section 3. In section 4 the dissociation of SO$_2$ molecule on the constructed Lie potential energy is obtained.

Lie potential energy

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

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

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

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

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

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 SO$_2$.

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

The Lie Potential energy can be written as follows:

$$V_{LiePE}(q_1, q_2, \phi) = (A_1 + A_{12})N_1^2[2 - e^{-\beta_1(q_1 - q_{1e})}]e^{-\beta_1(q_1 - q_{1e})} + (A_2 + A_{12})N_2^2[2 - e^{-\beta_2(q_2 - q_{2e})}]e^{-\beta_2(q_2 - q_{2e})}$$

$$+ 2A_{12}N_1N_2\{ [2 - e^{-\beta_1(q_1 - q_{1e})}]e^{-\beta_1(q_1 - q_{1e})}[2 - e^{-\beta_2(q_2 - q_{2e})}]e^{-\beta_2(q_2 - q_{2e})} \}^{1/2} \cos\tilde{\alpha}(\phi - \pi)$$

$$+ \frac{1}{4}\lambda N_1 N_2 \{ (2e^{-\beta_1(q_1 - q_{1e})} + 2e^{-\beta_2(q_2 - q_{2e})} - 2e^{-\beta_1(q_1 - q_{1e}) - \beta_2(q_2 - q_{2e})} \cos\tilde{\alpha}(\phi - \pi)$$

$$-2[(2 - e^{-\beta_1(q_1 - q_{1e})})e^{-\beta_1(q_1 - q_{1e})}(2 - e^{-\beta_2(q_2 - q_{2e})}e^{-\beta_2(q_2 - q_{2e})}]^{1/2} \cos\tilde{\alpha}(\phi - \pi)\},$$

$$where \quad \tilde{\alpha} = |\alpha| \tag{3}$$

The Lie potential energy, V_{Lie} for SO_2 molecule in which the bond angle is frozen at equilibrium position. a) in bond distance, b) in natural coordinates is shown in Fig.1.
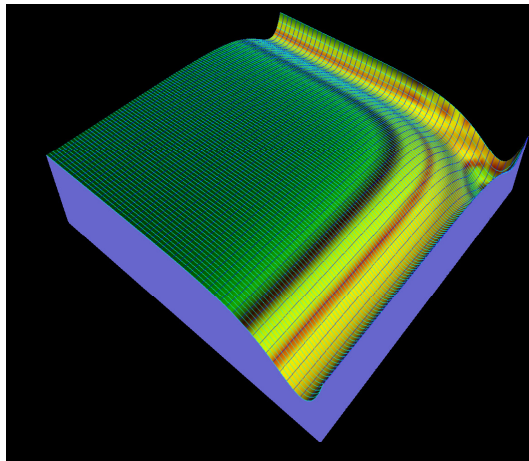
(a)
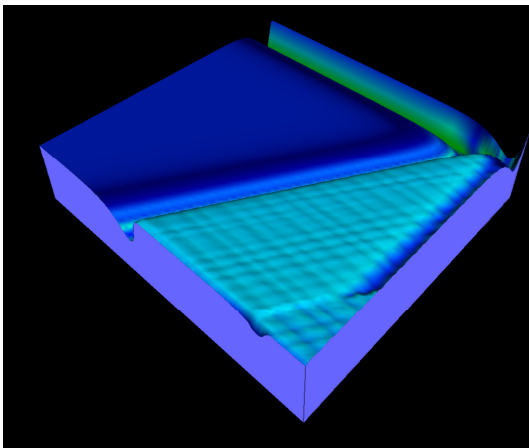
(b)

Fig.1. Plot of the Lie potential energy, VLie for SO₂ molecule. a) in bond distance, b) in natural coordinates.

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:

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

By introducing the natural coordinates q_1, q_2 it becomes:

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

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 SO$_2$ calculations, the time interval is Δt = 0.045 Femtosecond = 0.045×10^{-15} sec., and mesh spacing is $\Delta q_1 = \Delta q_2$ = 0.02 a.u. - the mesh normally contains ~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.

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 SO2 (LPE). We visualize the wave packet propagation at fixed times – to gain insight into the nature of the reaction process. Figure 2 shows 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. 2b. The wave packet has also clearly broadened. In Fig. 2c (time-step 3000), the wave packet is just entering the interaction region and has more than one peak. At time step 3800 (Fig. 2d) 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 3500Δt, 4000Δt, (Fig. 2) show the packet spreading and entering the interaction region. At time steps 50000, 6000, 7000, Fig. 2 shows 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 potential energy ranges from 2000 to 4000 time steps, the higher the collision energyis the lower the time threshold is. 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 = 1.3 eV the dissociation probability is 0.25.
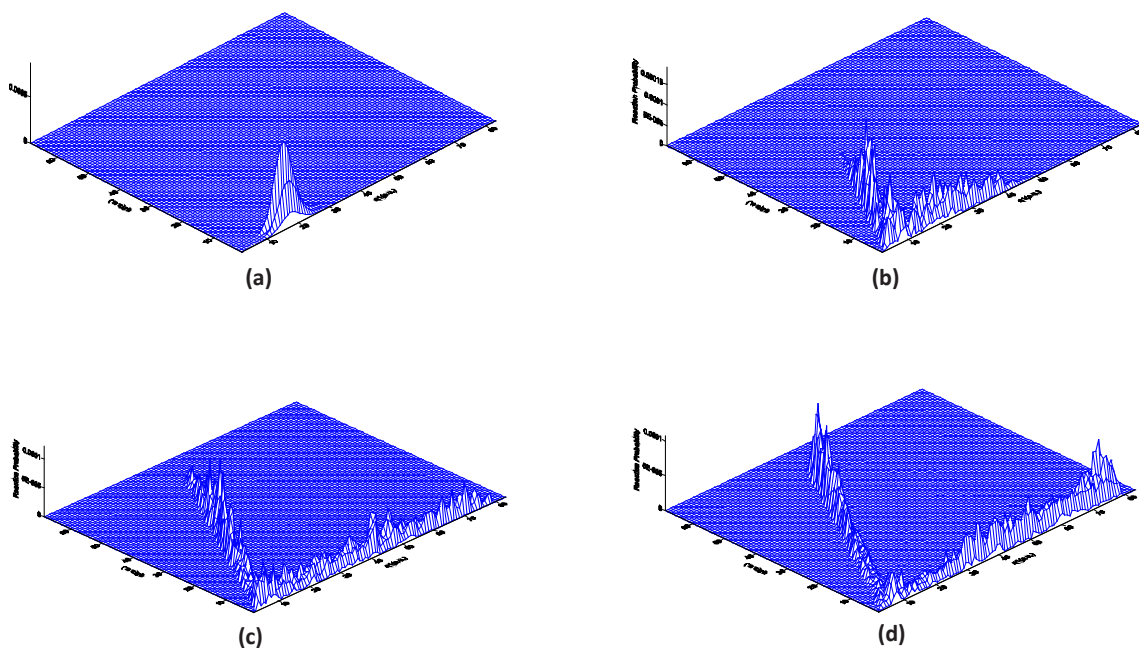

(a)

(b)

(c)

(d)

Fig.2. Dissociation probability for the collinear SO$_2$ reaction on the Lie potential energy for the case v = 0, E$_{trans}$.
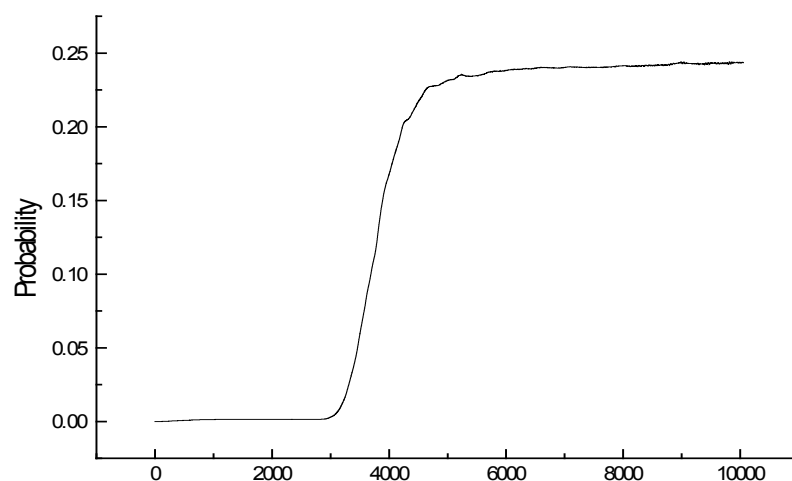**= 1.3 eV. (One time step Δt = 0.025 Femtosecond.).**

Fig.3. Plot of the Dissociation probability versus time for the collinear SO2 reaction on the Lie potential energy for the case υ = 0, E$_{trans.}$ = 1.3 eV. (One time step Δt = 0.025 Femtosecond.).

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ميكانيزم تحلل جزىء SO₂ باستخدام طرق جبرية

محمد حسن طلعت ،على حلمى موسى ، مصطفى اسماعيل شلبى ، وليد شحاتة صادق و محمد تاج الدين كمال

¹ قسم الفيزياء ـ كلية العلوم ـ جامعة عين شمس ـ القاهرة و²قسم الفيزياء النظرية ـ المركز القومى للبحوث ـ الجيزة ـ مصر

تم تطبيق معادلة شرودنجر المعتمدة على الزمن على تفاعل so2 و اجراء حسابات تفصيلية على الجهد السطحى الخاص بالتفاعل الذى تم انشاءه باستخدام جبر ليو. الجهد السطحى بمتلك تحويلات بين زوايا الاحداثيات و زوايا الروابط الجزيئية لوصف حركة الجزيئات كما توضح النتائج.