Intramolecular and dissociation dynamics of triatomic molecules: Some results for HCN and CO₂

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Abstract. Intramolecular dynamics of two linear molecules HCN and CO₂ are studied by computing trajectories, plotting Poincaré sections and calculating Lyapunov exponents. The process of dissociation is then studied by the same technique for HCN in the presence of a strong CO₂ laser. Results of these preliminary calculations unequivocally show a threshold intensity for dissociation which is possible to verify experimentally.

Keywords. Intramolecular dynamics; dissociation probability; triatomic molecules; Poincaré sections; Lyapunov exponent.

1. Introduction

How much of intramolecular dynamics is understood by performing computations of trajectories integrating the Hamiltonian equation of motion? It turns out that a lot can be learned and the limitations are quite often that of not having enough computer time to carry through all that you would want to do.

In this article, we use some recently utilized and accurate model Hamiltonians for the molecules CO₂ and HCN and examine what classical mechanics can say regarding these molecules. The results are relevant for two cases. In § 2, some results of computation of trajectories in the configuration space of vibrational motion of these molecules are presented utilizing Poincaré sections. The qualitative change in the dynamics on increasing the energy of the molecules is well understood by these computations. The dynamics can thereby be related to the theory of chaos and clear transitions from periodic regular trajectories to non-periodic irregular trajectories are seen. It is difficult to accurately quantify the transition energy by computing the trajectories and examining the Poincaré sections. A much better but (computationally) quite expensive method is to calculate the Lyapunov exponents for these trajectories. The change of sign of the Lyapunov exponent with variation of the energy of the system lets one obtain more accurate values of the transition energy. The results of these are discussed in § 2.

The success of the implementation of our own routine for the computation of the trajectories induced us to consider the dynamics of dissociation of these molecules stimulated by an external electromagnetic field. The problem is discussed in § 3 where

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the first results of these computations are presented. This new technique has now been implemented for the first time to discuss the intramolecular dissociation dynamics as well as to obtain the dissociation probability. It appears to be a rather promising technique especially in view of the near impossibility of obtaining any accurate quantum-mechanical photodissociation probability due to the prohibitive expense of the relevant computation. The threshold field strength of dissociation for HCN has been obtained with an accuracy which should be compared both with theoretical and with eventually experimental methods.

2. Intramolecular dynamics

The Hamiltonian model for CO₂ molecule is given by:

$$H = H_1 + H_2 + H_{12}, \quad (1)$$

with

$$H_i = (P_i^2/2\mu_i) + V(R_i), \quad i = 1, 2, \quad (2a)$$

$$H_{12} = (1/m_C)P_1P_2, \quad (2b)$$

$$V(R_i) = D(1 - \exp(-\alpha R_i))^2, \quad (2c)$$

where $D = 5.5 \text{ eV}$ and $\alpha = 3.1 \text{ \AA}^{-1}$.

In the above equation, R_i is the displacement of the CO bond from its equilibrium position, P_i is the conjugate momenta corresponding to R_i , $1/\mu_i = 1/m_C + 1/m_O$, m_C is the mass of the central atom (carbon mass), m_O is the oxygen mass and i refers to the specific bond in the molecule. These bonds are not equivalent if all the three masses are different. H_i is the Hamiltonian for the reduced mass μ_i consisting of the kinetic energy $P_i^2/2\mu_i$ and the potential $V(R_i)$ which depends only on the position R_i . The term H_{12} is the coupling between the motion of the two reduced masses (Wilson *et al* 1955). Since the molecules are linear, we assume that the angle between the two relevant bonds is 180° . Regardless of the choice of the potentials $V(R_i)$, the coupling term H_{12} is exact and plays a crucial role in our consideration. Such a model, while deficient in many respects such as absence of rotation, bending motion, Fermi resonance etc., is still capable of generating a good number of the vibrational levels of the molecule and therefore has been utilized for various studies in the literature (Buch *et al* 1982; Halonen and Child 1982; Terasaka and Matsushita 1985; Botschwina 1988; Karrlein 1991; Shi and Rabitz 1991).

For HCN, the Hamiltonian (Smith *et al* 1991) has given the same form as (1) and (2), with

$$V(R_i) = V_{i1}Z_i^2 + V_{i2}Z_i^3 + V_{i3}Z_i^4, \quad i = 1, 2, \quad (3a)$$

$$Z_i = 1 - \exp(-\alpha_i R_i), \quad (3b)$$

and the term H_{12} , however, is chosen to be

$$H_{12} = -(1/m_C)P_1P_2 + V(R_1, R_2), \quad (3c)$$

where

$$V(R_1, R_2) = V_1Z_1Z_2 + V_2Z_1^2Z_2 + V_3Z_1^2Z_2. \quad (3d)$$

All the parameters are given in table 1 and the indices 1 and 2 correspond to CN and CH coordinates, respectively. These parameters approximately fit the first 40 stretching vibrational levels in the spectrum with an error of about 0.01% of the energy values and predict the two possible dissociation pathways associated with this molecule within 15% for the channel (H + CN) and within 8% for the channel (HC + N) (Smith *et al* 1991).

The Hamiltonian equations of motion along with conservation of energy, give rise to a set of three coupled equations for each of these two Hamiltonians. These are then integrated generating the trajectories and the results are plotted as Poincaré sections with the coordinate R_2 and the momentum P_2 as the variables. Figures 1 and 2 show a set of these for CO₂ and HCN respectively. These are in ascending order in energy and even a cursory perusal of them shows how the trajectories make the transition from being periodic to chaotic as the energy is increased. A more

Table 1. Parameters for the generalized Morse potential for HCN (Smith *et al* 1991).

$\alpha_{\text{CN}} = 2.306172 \text{ \AA}^{-1}$	$\alpha_{\text{CH}} = 1.847393 \text{ \AA}^{-1}$	$V_1 = 0.30763 \text{ ev}$
$V_{11} = 10.99446 \text{ ev}$	$V_{21} = 5.69714 \text{ ev}$	$V_2 = -9.425 \times 10^{-6} \text{ ev}$
$V_{12} = 0.499332 \text{ ev}$	$V_{22} = 0.47528 \text{ ev}$	$V_3 = 3.657 \times 10^{-4} \text{ ev}$
$V_{13} = 5.954 \times 10^{-3} \text{ ev}$	$V_{23} = 8.426 \times 10^{-3} \text{ ev}$

Figure 1. Poincaré section at different values of energy for the CO₂ molecule where the two atoms of oxygen are 18 amu. (a) 1.5, (b) 2.5, (c) 3.0 and (d) 3.5 eV.

Figure 2. Poincaré section at four values of energy for the molecule DC^{16}N . (a) 2, (b) 3, (c) 4 and (d) 5 eV.

Table 2. Lyapunov exponent at different values of the energy.

	Energy (eV)	Lyapunov exponent
CO_2	2.50	-1.0
	2.76	-0.2
	3.00	0.5
HCN	2.00	-1.5
	2.80	-0.1
	2.90	0.3

quantitative estimate of the energy where such a transition occurs (threshold energy) requires rather extensive calculations involving computation of the Lyapunov exponent (Benettin *et al* 1976; Shimada and Nagashima 1979; Wolf *et al* 1985; Meyer 1986). Table 2 indicates where that occurs for $^{12}\text{C}^{16}\text{O}_2^1\text{H}^{12}\text{C}^{14}\text{N}$, respectively.

There are two remarks that need to be made and which are generally applicable. First, even the simplest of couplings $-P_1 P_2 / m_c$ is able to create the transition to chaos from elementary models of vibrational dynamics. Therefore, we expect, in

general, to see manifestation of transition to chaos at some energy for all polyatomic molecules in their vibrational motion. Second, chaotic dynamics is strongly and sensitively dependent on the isotopic mass chosen for the molecule (Pichierri 1992; Botina *et al* 1993).

These computations have served as a starting point for calculation dissociation probability of HCN by intense laser fields utilizing trajectories and Poincaré sections and to investigate the relationship between the threshold energy for chaotic dynamics and the dissociation probability brought about by the external electromagnetic field.

3. Dissociation dynamics of HCN

We employed the same type of method described in the previous section to study the laser-induced dissociation of HCN molecule. The laser field is characterized by the electric field strength and frequency of the laser light. Interaction between the molecule and the laser radiation field is included through the dipole moment function. The Hamiltonian for the laser-molecule interactions is

$$H_I = E_0 \mu(\mathbf{R}) \cdot \cos(\omega t), \quad (4)$$

where E_0 is the electric field strength, μ is the dipole moment, t is the time, and ω is the frequency of the laser. The dipole function was taken as

$$\mu = (R_{CH}, R_{CN}) = A [(R_{CN} + R_{CN,eq}) \exp(-\beta R_{CN}) - (R_{CH} + R_{CH,eq}) \exp(-\beta R_{CH})], \quad (5)$$

where A is a constant proportional to the permanent dipole of the molecule in its

Figure 3. Classical probability of dissociation in function of the electric field strength (ev/Å) where the frequency of the laser is 0.114 ev. The number of initial conditions is 20.

Figure 4. Poincaré section at different values of the electric field strength where the frequency of laser is 0.114 eV for the molecule of HCN. (a) 5, (b) 10, (c) 15, (d) 18 and (e) 19 $\text{ev}/\text{\AA}$.

equilibrium, R_i is the displacement from the equilibrium position, $R_{i,eq}$, of each bond i , and β is a constant that is taken equal to one. We expect this dipole function to be a good approximation because the force constants of C–H and C–N are not very different from the corresponding force constants in HCN (Smith *et al* 1987; Botschwina 1988).

In order to study the laser-induced dissociation probability of the HCN molecule, it is necessary to calculate the classical probability of dissociation starting from a set

Table 3. Lyapunov exponent and the maximum value of energy reached at different values of the electric field strength where the frequency of laser is 0.114 eV for the molecule of HCN. At 19 eV/Å there is dissociation.

Electromagnetic strength (ev/Å)	Lyapunov exponent
5	0.0050
10	0.0224
15	0.0327
18	0.0500
19	0.2500

of initial conditions at a specific energy. The probability is given by

$$P_{\text{diss}}(R, T) = \frac{1}{N} \sum_{i=1}^N \delta(R_i(T)), \quad (6)$$

where N is the number of initial conditions, T is the optical cycle, R is the deviation of the relevant bond (CN or CH) from its equilibrium position and δ function is defined as

$$\delta(R_i) = \begin{cases} 1, & \text{if } R_i \geq R_{\text{diss}} \\ 0, & \text{if } R_i < R_{\text{diss}} \end{cases}, \quad (7)$$

and R_{diss} is taken equal to 9 Å (at this value the potential energy = 1×10^{-5} eV). The results are given in figure 3 where we show the classical probability as a function of the field strength E_0 (eV/Å) for the reactions, $\text{HCN} \rightarrow \text{H} + \text{CN}$ and $\text{H} + \text{CN} \rightarrow \text{H} + \text{C} + \text{N}$. It is clear from figure 3 that the threshold field strength for the dissociation of $\text{HCN} \rightarrow \text{H} + \text{CN}$ has a value of 18.16 eV/Å.

In figure 4 we show the same Poincaré section (i.e. for R_2 and P_2) at different values of field strength and a frequency of 0.114 eV. These are for field strengths: (a) 5 eV/Å, (b) 10 eV/Å, (c) 15 eV/Å (d) 18 eV/Å and (e) 19 eV/Å. At the last field strength (figure 4e), we have already calculated that the dissociation probability of the molecule is equal to 0.40 for the reaction $\text{HCN} \rightarrow \text{H} + \text{CN}$ and 0.20 for the reaction $\text{H} + \text{CN} \rightarrow \text{H} + \text{C} + \text{N}$ (figure 3). From these figures, we see that at the lowest field strength i.e. at 5 eV/Å, the Poincaré section is confined to an almost circular region. With increase of field strength, qualitative changes appear; however, it is difficult to conclude much regarding dissociation from these figures.

Lyapunov exponents at different values of electromagnetic field strength are shown in table 3. At 19 eV/Å, even though the molecule dissociates, one can still calculate the Lyapunov exponent as long as the calculation is limited to not very long time periods. The values of the Lyapunov exponent jumps from 0.05 at 18 eV/Å to 0.25 for 19 eV/Å. Therefore one sees that dissociation may be related to deterministic chaos (Smith *et al* 1987; Botschwina 1988).

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