Transition from Regular to Stochastic Vibrational Motion in H_3^+ Molecule: An ab initio Classical Trajectory Study

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An ab initio classical trajectory study of intramolecular vibrational dynamics in H_3^+ molecule revealed a transition from regular quasiperiodic to stochastic motion at an energy slightly higher than the zero point vibrational energy.

Key words: H_3^+ Molecule; Vibrational Dynamics; ab initio Stochastic Motion.

How energy moves around between the vibrational modes of a polyatomic molecule is of considerable interest, both spectroscopically and theoretically. Historically the most widely known studies of intramolecular vibrational energy redistribution are associated with thermal unimolecular reactions [1]. In the developing unimolecular reaction rate theory, Slater [2] described the excited molecule as an assembly of harmonic oscillators with forbidden energy sharing between vibrational modes. In contrast, the Rice-Ramsperger-Kassel-Marcus (RRKM) [3] theory assumes that the excitation energy randomizes rapidly and is distributed statistically among all modes. At the same time, Fermi, Pasta, and Ulam [4] performed numerical simulation of energy sharing in a simple chain of coupled nonlinear oscillators. The result, known as FPU-paradoxon, was surprising, showing very little relaxation and thus demonstrating that the dynamics of energy sharing in this model can be far from straightforwad and need not be statistical at all. This lack of ergodicity was explained by Ford [5], showing that the frequencies of the normal modes of FPU systems do not fulfill the resonance conditions (integer ratios between them). Full connection between resonances and ergodicity was revealed by the Kolmogorov-Arnold-Moser (KAM) theorem [6].

The strong coupling and many resonances in even small molecules, i.e. the possible existence of FPU-like behavior in molecular systems has been an intriguing and persistent question for a long time [7].

The aim of the present study is to show for a simple polyatomic molecule, H_3^+, that its vibrational dynamics exhibit similar features a those observed in FPU-systems. This molecule was chosen for three reasons: i. Only two electrons allow us to perform extensive ab initio calculations; ii. H_3^+ is known to be a strongly anharmonic (floppy) molecule with large amplitude motion. Therefore strong coupling between vibrational modes is expected; iii. This molecule has two degenerate deformation modes, ω_1 and ω_2, of symmetry e' with frequency 2521 cm^{-1} (period 11.3 fs) and one ring breathing mode ω_3 of symmetry a_1' with frequency 3178 cm^{-1} (period 9.1 fs) [8]. Therefore we have the resonance condition $\omega_1/\omega_2 = 1$.

The equilibrium structure of H_3^+ (equilateral triangle) as well as its vibrational normal modes were calculated at the HF/6-311G** level $\omega_1 = \omega_2 = 2942$ cm^{-1}, $\omega_3 = 3660$ cm^{-1}. Ab initio classical trajectory calculations were performed with DRP routine [9] as implemented in the GAMESS program [10]. At each time step, the energy and energy gradient for each atom were calculated at HF/6-311G** level, and the position and velocity vectors for the next step were extrapolated by the Taylor expansion according to Newton's law [11]. The time step was 0.05 fs in all calculations. Direct combination of an ab initio electronic structure calculation with classical dynamics is an integrated approach which bypasses the construction of the potential energy surface.

In Fig. 1, the time dependencies of all three normal mode coordinates are shown. As can be seen, in the ground state, when the motion possesses just the zero-point vibrational energy $\sum_{i=1}^{3} \frac{1}{2} \hbar\omega_i$ (Fig. 1a), the vibrational motion is regular. At higher energies supplied to the vibrational modes (Fig. 1b–d), a complicated non-

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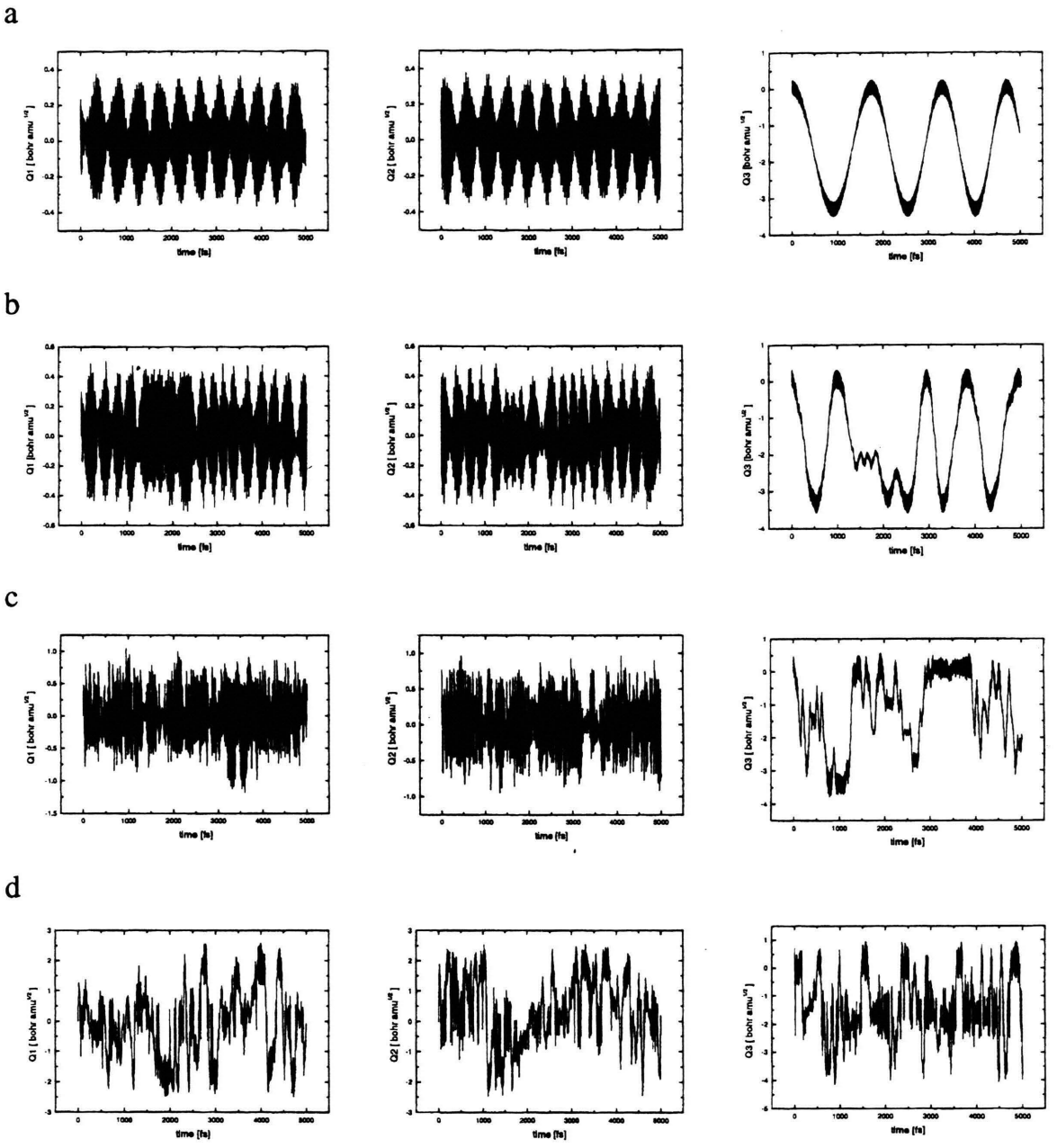

Fig. 1. Time dependences of the normal mode coordinates Q_1, Q_2, and Q_3 for various amounts of excitation energy $\alpha \sum_{i=1}^{3} \hbar\omega_i$, supplied to the normal modes: a $\alpha = 0.5$ (zero point vibrational energy); b, $\alpha = 0.75$; c, $\alpha = 1.5$; d, $\alpha = 2.5$.

periodic character occurs. The threshold energy of this transition lies at an energy close to $\sum_{i=1}^{3} 0.7\,\hbar\omega_i$. The calculations are very time consuming (for the construction of Fig. 1 more than one million energy and energy gradient calculations were needed). Therefore it is not easy to get more precise results.

The behavior of the H_3^+ molecule resembles not only the FPU-model, but also the dynamics of astrophysical systems described by the Henon-Heiles Hamiltonian [12].

Our results represent just the first step in understanding the interplay between the regular and stochastic molecule dynamics without resorting to a simplified model Hamiltonian.

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[1] P. J. Robinson and K. A. Holbrook, Unimolecular Reactions, Wiley & Sons, New York 1972.
[2] N. B. Slater, Theory of Unimolecular Reactions, Cornell University Press, Ithaca 1959.
[3] R. A. Marcus, J. Chem. Phys. **20,** 359 (1952).
[4] E. Fermi, J. R. Pasta, and S. M. Ulam, Los Alamos Scientific Laboratory Report LA – 1940 (1955); also reprinted in Collected Works of Enrico Fermi, Vol. II, University of Chicago Press, Chicago 1965.
[5] J. Ford, Adv. Chem. Phys. **24,** 155 (1973).
[6] V. I. Arnold, Russian Math. Survey **18,** 85 (1963).
[7] T. Uzer and W. H. Miller, Phys. Rep. **199,** 73 (1991).
[8] L. J. Lembo, A. Petit, and H. Helm, Phys. Rev. A **39,** 3721 (1989).
[9] M. S. Gordon, G. Chaban, and T. Taketsugu, J. Phys. Chem. **100,** 11512 (1996).
[10] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, and T. L. Windus, J. Comput. Chem. **14,** 1347 (1993).
[11] J. J. P. Stewart, L. P. Davis, and L. W. Burggraf, J. Comput. Chem. **8,** 1117 (1987).
[12] M. Henon and C. Heiles, Astron. J. **69,** 73 (1964).