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Periodic motions due to nonlinearity: the regular vibrational dynamics of chaotic DCN

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Abstract

Periodic motions due to nonlinear resonances of D–C and C–N stretches of DCN molecule are shown by an algorithm based on coset representatives. These motions are highly localized on either D–C or C–N bond, or that their action ratios on D–C and C–N are 2:3 or 1:1. These periodic motions bear peculiar characters not possessed by the normal modes based on the harmonic approximation. It is shown that chaotic motion is mainly due to the D–C stretch. However, quasiperiodic modes of highly localized D–C stretch are also identified.

Keywords: Highly excited molecular vibration; Periodic motions; Nonlinearity

1. Introduction

Highly excited molecular vibration can be viewed as a (semi) classical nonlinear many-body system due to its high excitation and multiple resonances among the bond motions. An interesting and essential topic is the application of nonlinear dynamics [1] to molecular vibration. For this, an algorithm based on the coset representatives has been developed to unfold the molecular vibrational dynamics, in contrast to the traditional method by Schrödinger equation [2–6]. This algorithm treats the dynamics as the trajectories in the coset (phase) space. Thereby, knowledge and techniques in nonlinear dynamics such as the KAM [7] (Kolmogorov, Arnold, Moser) theorem and the Lyapunov exponent [8], etc. can find their places in the study of molecular dynamics. This is a powerful algorithm that it bridges the gap between the nonlinear science and molecular spectroscopy. It is also noted that algebraic approach to molecular vibration is not unique. Iachello and Levine has also developed an algebraic method based on the chain structures of groups [9].

Nonlinearity causes chaos, in general. However, it may also cause periodicity which is different from the periodicity by linearity with more variations. The nonintegrable dynamics by the noted KAM theorem is that it is full of chaotic trajectories, especially for higher levels of which the resonances are strong enough to destroy most periodic and/or quasiperiodic trajectories. Though the remnant periodic trajectories are scarce, they are not to be neglected that they form the invariant skeleton of the phase (coset) space. It is noticeable that Gutzwiller has been successful in giving a trace formula which relates the quantum density of states as a sum over periodic orbitals [7].

The DCN vibrational dynamics is such a case. Its chaotic aspects have been touched in our previous work [10] with the exposition of the period-3 trajectories which are embedded in the chaotic 'sea'. By this and Gutzwiller's idea, we perceive that periodic trajectories can play important roles in a chaotic system, though at a first glance, they are different from the chaotic trajectories in essence. With this motivation, periodic trajectories of this chaotic DCN system were explored numerically to demonstrate their characters in this work. It needs emphasis that the periodicity mentioned here is a result of nonlinearity which is different from that of normal modes by the harmonic approximation [11]. Trajectories with various periods were

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identified with peculiar characters not found in the frame work of normal mode analysis. Apparently, this kind of work will enrich our understanding of the nonlinear aspects of vibrational dynamics and its implication in molecular spectroscopy deserves attention.

2. The coset dynamics of DCN

The two Morse-type stretches of D–C and C–N bonds of DCN with 1:1 and 2:3 resonances form a prototype for the nonlinear molecular vibration. The resonances were elucidated from the fit of an algebraic Hamiltonian to the DCN experimental spectra [12] of which the bend motion is decoupled by the Marguardt method [13]. The algebraic Hamiltonian is composed of three parts [14]:

$$H_0 = \omega_s\left(n_s + \frac{1}{2}\right) + \omega_t\left(n_t + \frac{1}{2}\right) + X_{ss}\left(n_s + \frac{1}{2}\right)^2 + X_{tt}\left(n_t + \frac{1}{2}\right)^2 + X_{st}\left(n_s + \frac{1}{2}\right)\left(n_t + \frac{1}{2}\right)$$

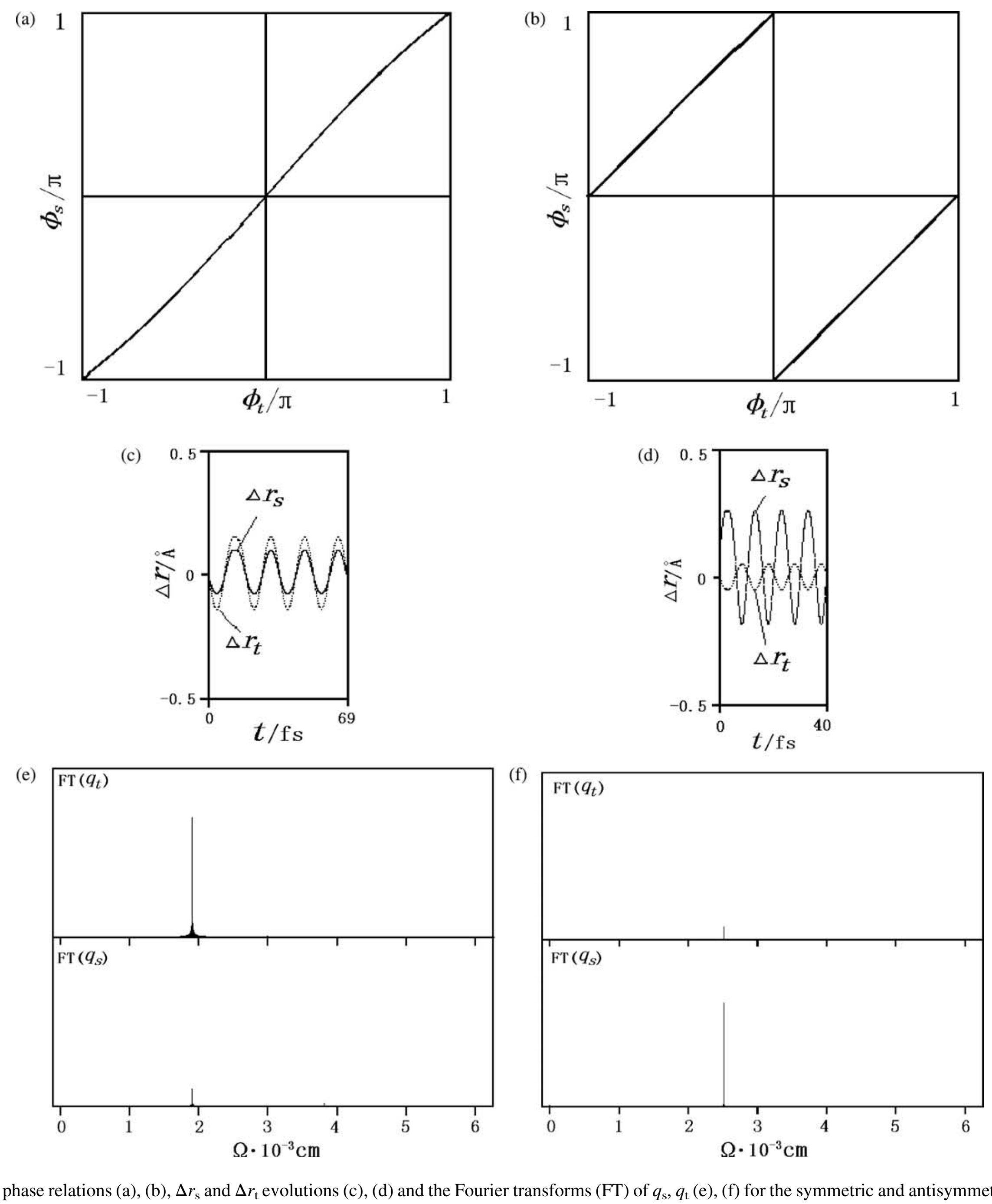

Fig. 1. The phase relations (a), (b), Δr_s and Δr_t evolutions (c), (d) and the Fourier transforms (FT) of q_s, q_t (e), (f) for the symmetric and antisymmetric period-1 trajectories, respectively.