VIBRATIONAL CHAOS IN KCN: A COMPARISON OF QUANTUM AND CLASSICAL CALCULATIONS

Jonathan TENNYSON
Science and Engineering Research Council, Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK

and

Stavros C. FARANTOS
Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Vas. Constantinou Ave. 48, Athens 116/35, Greece

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Comparisons between classical and quantum-mechanical calculations on the vibrational states of the floppy KCN molecule using a realistic potential are made. Classical chaos is observed even below the quantum ground state. Analysis of the quantum nodal structure, avoided crossings and level spacing distribution all point to an early onset of quantum chaos, although some quantum "sluggishness" is observed.

1. Introduction

The transition from regular (quasiperiodic) to chaotic motion observed in classical dynamical systems is now well known. It has triggered an intensive investigation to find a quantum analog of classical chaos [1–12]. This subject has recently been reviewed by Reinhardt [13].

The characterization of a classical trajectory as quasiperiodic or chaotic is usually accomplished by studying (a) Poincaré surfaces of section or the projection of the trajectory in a coordinate plane, (b) the power spectrum of a dynamical variable, and (c) by computing the rate of exponential divergence of two initially adjacent trajectories. The latter quantity provides a measure of chaos and it has been shown by numerical experiments that it is related to the characteristic time for energy randomization in the system [14–16].

In the case of quantum dynamics the energy levels and the topography of wavefunctions have both been used to establish criteria for quantum chaos [13]. It has been shown that at energies where the phase space is occupied by quasiperiodic trajectories the wavefunction is localized on the coordinate space with amplitude maxima on the classical caustics [1]. Hose and Taylor [2] have proposed as a criterion for the assignment of a regular state the appearance of a coefficient in the expansion of the wavefunction the square of which is greater than 0.5. However this criterion is limited since it does not imply chaos when it is not satisfied. In the chaotic regions of phase space the wavefunction is spread over all configuration space [1]. Furthermore the complicated nodal structure of the wavefunction found for these states has also been used as a criterion for quantum chaos [3]. On the other hand regular states show an ordered nodal pattern that can be used to assign good quantum numbers.

Marcus and co-workers [4–6] have suggested as a criterion of quantum chaos the appearance of multiple avoided crossings in energy level diagrams constructed by varying a parameter in the Hamiltonian. In the quasiperiodic regime there are only isolated avoided crossings. The different behaviour of the energy levels in the two regimes, quasiperiodic–chaotic, is also manifested in the different level spacing distributions. Berry and Tabor [17] have shown that for classical regular systems the distribution is completely random.

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It can be represented as a Poisson distribution

$$P = \exp(-S/\bar{S})/\bar{S}, \quad (1)$$

where S is the spacing between adjacent lines and $\bar{S}$ is the average value. It has been proposed that chaotic states obey a Wigner distribution [13]

$$P = (\pi S/2\bar{S}^2)\exp(-\pi S^2/4\bar{S}^2). \quad (2)$$

The criterion of level spacing distribution [7] is appealing as it can be applied to experimental results [8].

Most studies of quantum chaos have been restricted to two-dimensional model systems such as Hénon–Heiles type problems [13]. The conclusion of these studies is that classical chaos does not always imply quantum chaos.

Lehmann et al. [9] tried to correlate the experimentally observed vibrational spectrum of HCN with the results of classical dynamics on a real potential energy surface. They found that the chaotic behaviour of the dynamics was not in accordance to the simple and regular spectrum of HCN which they observed. Although comparison of classical or quantum theoretical results with the experiment is the ultimate goal, it is necessary first to carry out classical and quantum-mechanical studies on real potential energy surfaces. This is dictated firstly by the lack of a complete theory of quantum chaos. Secondly while solutions to a chaotic problem are completely determined by a given potential, small changes to this potential can be expected to change these solutions unpredictably. Thus comparison between experiment and theory by use of an imperfect surface is unlikely to be fruitful. Indeed, Lehmann et al. [10] found the classical onset of chaos to vary by a factor of nearly 3 between two similar surfaces.

If progress is to be made on quantum chaos, we believe, that it is necessary to study real systems using both quantum and classical mechanics and identical potentials. This view has recently been given strong support by Reinhardt [13].

In this article, which is the first in a series, we present results of classical and quantum calculations on KCN. The spectroscopy of this "floppy" molecule has recently excited much interest both experimentally [18,19] and theoretically [20–23]. In particular, the large-amplitude bending motion and the low barrier to linear KNC structure from the triangular equilibrium geometry stimulated the development of new theoretical methods for tackling floppy molecules [22]. We note that calculations have shown that KCN displays a complicated nodal pattern even a few quanta above the ground state [21]. KCN thus suggests itself as a suitable starting point for the study of vibrational chaos.

2. Classical calculations

Following the previous work on KCN, we freeze the CN bond. This is a physically motivated approximation because of high frequency of the CN vibration. Hence the problem is restricted to a two-dimensional world and we leave the three-dimensional case for future consideration.

We use the potential energy surface calculated ab initio by Wormer and Tennyson [24], which correctly predicts the observed triangular structure of KCN [19]. The potential is expressed as a function of the distance R, of K from the centre of mass of CN, and the angle ϑ, which is formed between R and the bond length of CN, r. A value of $r = 2.186\,a_0$ was assumed. Since we are interested in studying only vibrational excitations, we use the Hamiltonian appropriate to a rotationless molecule

$$H = p_R^2/2\mu_1 + (1/2\mu_1 R^2 + 1/2\mu_2 r^2)p_\vartheta^2 + V(R,\vartheta), \quad (3)$$

where μ_1 and μ_2 are the reduced masses of KCN and CN respectively, and p_i is the momenta conjugate to coordinate i. This is the classical analog of the body-fixed $J = 0$ Hamiltonian of Tennyson and Sutcliffe [22]. Hamilton's equations were integrated by an Adams–Moulton fifth-order predictor sixth-order corrector method initialised with a fourth-order Runge–Kutta procedure.

A characteristic measure of chaos is the maximal Lyapunov number calculated for a pair of trajectories as described previously [14,15]. This number tends to zero for quasiperiodic trajectories and to a positive value for chaotic trajectories. Generally, numerical calculations have shown that this quantity increases with the energy. We have obtained average values of the maximal Lyapunov number from batches of fifty trajectories in the energy range 207–1067 cm^{-1}. Initial conditions for the trajectories are chosen by using orthant sampling [25]. The results are shown in fig. 1. We note that for KCN chaos starts very early. Even 225 cm^{-1} above the absolute minimum of the surface at −39086.1 cm^{-1} (−4.85 eV) which corresponds to the

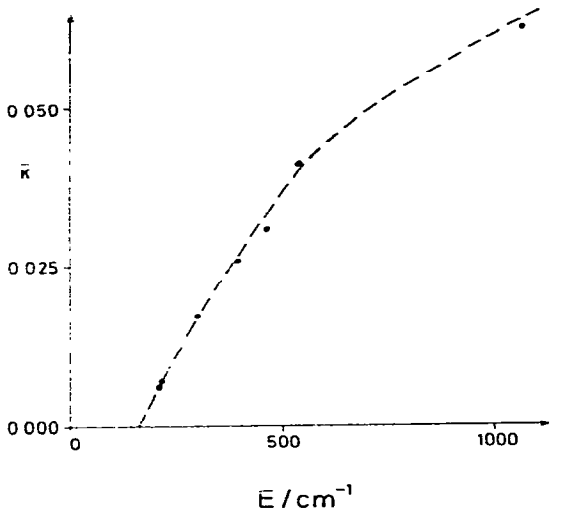

Fig. 1. The stochastic parameter for KCN, $\bar{\kappa}$ in reciprocal time units of about 10^{14} s^{-1}.

ground state, a substantial region of phase space is covered by chaotic trajectories. Study of individual trajectories started from the equilibrium geometry with the kinetic energy distributed between the stretching and bending modes confirms this. We examine for each trajectory: (a) the power spectrum of the momentum, (b) Poincaré surface of section and (c) the projection of the trajectory on the coordinate plane. Two examples are shown in fig. 2; all indicators show both trajectories to be chaotic. The second trajectory has an energy which is above the barrier (503.9 cm^{-1}) separating the symmetric minima of KCN. The trajectory is observed to ergodically fill the energetically available space.

3. Quantum calculations

Quantum-mechanical calculations were performed on KCN using the body-fixed method of Tennyson and Sutcliffe [22] and program ATOMDIAT [26]. Table 1 shows the convergence of the lowest 35 excited states with increasing basis set and gives details of the basis used. All results quoted below are for $J = 0$ with $n = 21$, $l = 30$, giving a basis of 651 functions, at which level the lowest 35 states are converged to 0.1 cm^{-1}.

Fig. 3 shows sample wavefunctions for 4 vibrational states of KCN. The ground, first excited and second excited (fig. 3a) states can be assigned unambiguously as the (0,0), (0,1) and (0,2) states, where we used the notation (v_{stretch}, v_{bend}). The third and fourth excited states (figs. 3b and 3c) cannot be assigned directly from their nodal structure. States above the fourth excited state show a complicated nodal pattern, see for example fig. 3d.

Following Marcus and co-workers [4–6], we have tested the effect of perturbing the KCN potential. To do this we perturbed the third term in the Legendre expansion of the potential:

$$V'(R, \vartheta) = V(R, \vartheta) + \delta V_2(R) P_2(\cos \vartheta), \qquad (4)$$

where $\delta = 0$ gives the unperturbed potential V. Fig. 4 depicts variations in the energy levels as a function of this perturbation. Despite the fact that we are only varying one term in the potential by ±3%, we find many avoided crossings, which occur with increasing frequency above the second excited state.

We have analysed the level spacing distribution for

Table 1
Convergence of the first 35 vibrationally excited states of KCN with basis set. All frequencies in cm^{-1} are relative to the ground state at −38861.4005 cm^{-1}

n [a]	l [b]	Excited state						
		5	10	15	20	25	30	35
21	30	314.538	530.235	688.891	838.635	949.607	1067.83	1173.97
23	30	314.538	530.234	688.890	838.602	949.606	1067.79	1173.95
21	32	413.538	530.235	688.890	838.634	949.594	1067.76	1173.89

[a] Number of Morse oscillator-like functions in the R basis with $R_e = 5.13\ a_0$, $D_e = 0.1777\ E_h$, $\omega_e = 0.0013\ E_h$ [26].
[b] Maximum l in Legendre polynomial basis for ϑ.

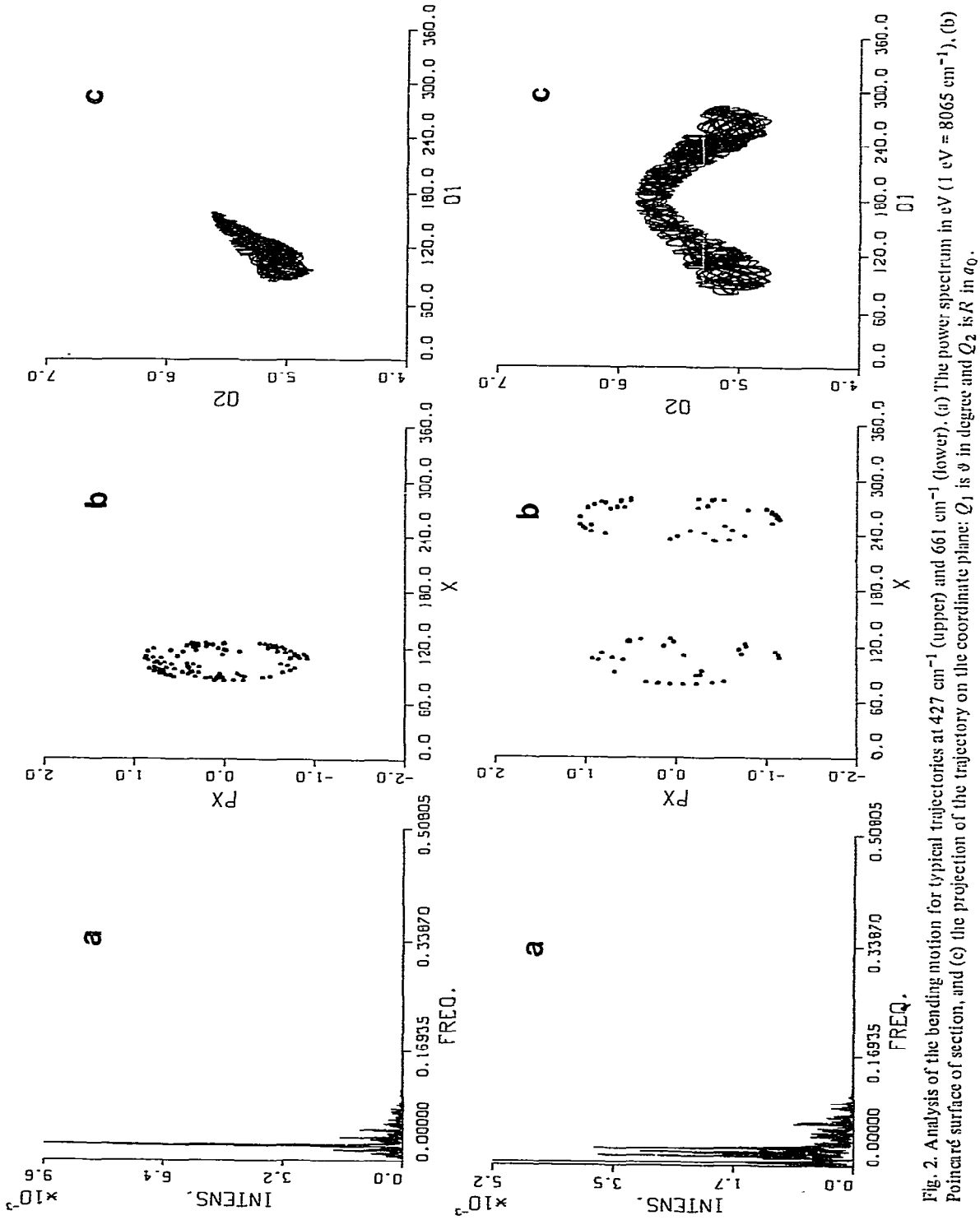

Fig. 2. Analysis of the bending motion for typical trajectories at 427 cm^{-1} (upper) and 661 cm^{-1} (lower). (a) The power spectrum in eV (1 eV = 8065 cm^{-1}), (b) Poincaré surface of section, and (c) the projection of the trajectory on the coordinate plane: Q_1 is ϑ in degree and Q_2 is R in a_0.

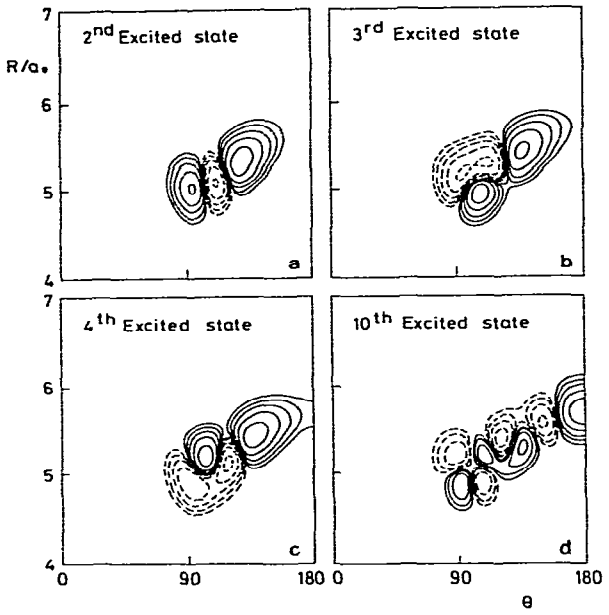

Fig. 3. Amplitudes of low-lying vibrational states of KCN. The contours link points where the wavefunction has 4%, 8%, 16%, 32% and 64% of its maximum amplitude. Solid curves enclose regions of positive amplitude and dashed lines of negative amplitude.

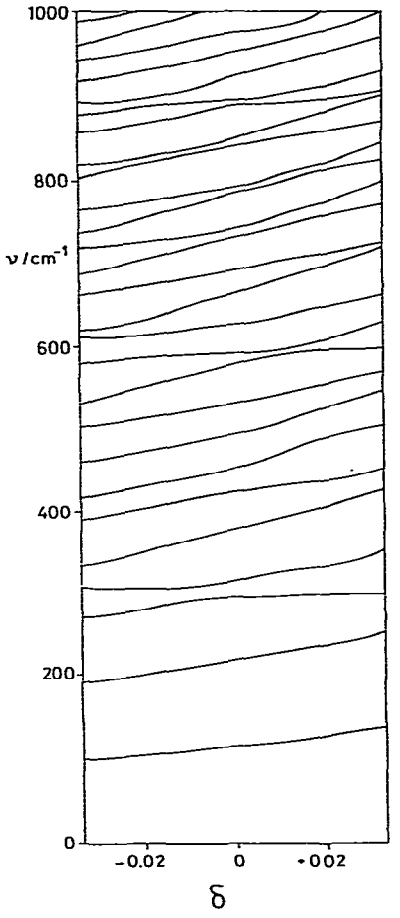

Fig. 4. Variation of vibration frequency with δ (see text). All frequencies are plotted relative to the vibrational ground state.

the 72 levels lying above the second excited state. They are approximately fitted by a Wigner distribution, which should represent chaotic states [13]. However, the small number of available states does not allow us to calculate a distribution with high statistical accuracy.

4. Discussion and conclusions

Analysis of the contour plots of the lowest 35 vibrational states has led us to the following conclusions. The ground and first two excited states are regular, none of the remaining states can be assigned from their nodal structure. However, the presence of what appears to be an isolated avoided crossing for $\delta \approx 0.0$ for the third and fourth excited states suggests that they could be regular states in resonance. This behaviour has recently been commented on by De Leon et al. [11].

The floppy molecule method which we apply yields no dominant coefficients for the near-harmonic low-lying states of KCN. It is thus not useful to apply the criterion of Hose and Taylor [2] to these calculations. However, previous calculations by Tennyson and Sutcliffe [20] on the vibrational states of KCN used a normal mode expansion to solve the Eckhart Hamiltonian. These results have since been shown to be unreliable for higher states because of the singularity encountered for linear geometries with this formalism [21]. Inspection of their results suggest that the ground and first three excited states should be classified as regular according to the criterion of Hose and Taylor. We can draw no conclusions about the states above these because of the increased importance of linear geometries in these higher states.

The complicated nodal structure, the appearance of frequent avoided crossings and perhaps the Wigner-

like spectral distribution all suggest chaotic behaviour above the fourth excited state. Classically a substantial region of phase space is occupied by chaotic trajectories even when they are below the zero point energy. Thus for both quantum and classical mechanics KCN displays chaotic behaviour at surprisingly low energies when comparison is made with other strongly bound molecules [10,14].

However, the transition from regular to chaotic behaviour occurs later in the quantum results. This phenomenon, called quantum "sluggishness", can be explained by the large spacing (relative to $\hbar$ [6]) of the low-lying levels. It has recently been observed in the "stadium problem" [27].

In conclusion, the early onset of chaos in both quantum and classical calculations suggests at least qualitative agreement between the two methods.

This early occurrence of chaos in KCN, with its strongly anharmonic potential and low barrier to linearity, has led us to investigate other floppy systems in a similar manner. In particular, LiCN is known to support relatively low-lying vibrational states with irregular nodal structure [28]. In a future publication we will analyse the behaviour of LiCN and hence the criteria that we have used here for establishing quantum chaos [29].

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References

[1] D.W. Noid, M.L. Koszykowski and R.A. Marcus, J. Chem. Phys. 71 (1979) 2864.
[2] G. Hose and H.S. Taylor, J. Chem. Phys. 76 (1982) 5356.
[3] R.M. Stratt, N.C. Handy and W.H. Miller, J. Chem. Phys. 71 (1979) 3311.
[4] D.W. Noid, M.L. Koszykowski and R.A. Marcus, Chem. Phys. Letters 73 (1980) 269.
[5] R. Ramaswamy and R.A. Marcus, J. Chem. Phys. 74 (1981) 1379.
[6] R.A. Marcus, J. Chem. Soc. Faraday Discussions 75 (1983), to be published.
[7] T. Matsushita and T. Terasaka, Chem. Phys. Letters 105 (1984) 511.
[8] E. Abramson, R.W. Field, D. Imre, K.K. Innes and J.L. Kinsey, J. Chem. Phys. 80 (1984) 2298.
[9] K.K. Lehmann, G.J. Scherer and W. Klemperer, J. Chem. Phys. 77 (1982) 2853.
[10] K.K. Lehmann, G.J. Scherer and W. Klemperer, J. Chem. Phys. 78 (1983) 608.
[11] N. De Leon, M.J. Davis and E.J. Heller, J. Chem. Phys. 80 (1984) 794.
[12] J.S. Hutchinson and R.E. Wyatt, Phys. Rev. A23 (1981) 1567.
[13] W.P. Reinhardt, in: The mathematical analysis of physical systems, ed. R. Mickens (Van Nostrand, Princeton, 1984).
[14] S.C. Farantos and J.N. Murrell, Chem. Phys. 55 (1981) 205.
[15] S.C. Farantos, Chem. Phys. Letters 92 (1982) 379.
[16] S.C. Farantos, J. Phys. Chem. 87 (1983) 5061.
[17] M.V. Berry and M. Tabot, Proc. Roy. Soc. A356 (1977) 375.
[18] P. Kuijpers, T. Töring and A. Dymanus, Chem. Phys. Letters 42 (1976) 423.
[19] T. Töring, J.P. Bekooy, W.L. Meerts, J. Hoeft, E. Tiemann and A. Dymanus, J. Chem. Phys. 73 (1980) 4875.
[20] J. Tennyson and B.T. Sutcliffe, Mol. Phys. 46 (1982) 97.
[21] J. Tennyson and A. van der Avoird, J. Chem. Phys. 76 (1982) 5710.
[22] J. Tennyson and B.T. Sutcliffe, J. Chem. Phys. 77 (1982) 4061.
[23] G. Brocks, J. Tennyson and A. van der Avoird, J. Chem. Phys. 80 (1984) 3223.
[24] P.E.S. Wormer and J. Tennyson, J. Chem. Phys. 75 (1981) 1245.
[25] D.L. Bunker and W.L. Hase, J. Chem. Phys. 59 (1973) 4621.
[26] J. Tennyson, Computer Phys. Commun. 29 (1983) 307.
[27] M. Shapiro, R.D. Taylor and P. Brumer, Chem. Phys. Letters 106 (1984) 325.
[28] G. Brocks and J. Tennyson, J. Mol. Spectry. 99 (1983) 263.
[29] S.C. Farantos and J. Tennyson, to be submitted.