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ROUTES TO VIBRATIONAL CHAOS IN TRIATOMIC MOLECULES

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Analysis of both classical and quantum calculations on LiNC and LiCN shows the onset of vibrational chaos is closely associated with the degree of bending excitation. Conversely quasiperiodic stretching states persist above the barrier to isomerization. Classical studies on O_3 give similar results. In the light of these results we re-interpret the high-energy vibrational data on O_3 and HCN and suggest that the observed regular stretching states probably are embedded in the chaotic region. We discuss the importance of mode coupling by the potential.

1. Introduction

Recently Hose and Taylor [1] have analysed the phenomenon of mode localization in highly excited vibrational states. They argue that overtone states have a stability not displaced by combination states, and thus can exist as mode localized (quasiperiodic) states embedded in the mode mixed (chaotic) quasicontinuum. They use this argument to explain a variety of experimental data on polyatomics in high-lying vibrational states.

Triatomics are the simplest molecules that can display vibrational chaos. Conventionally their localized vibrational states are labeled as (v_1, v_2, v_3), where v_1 and v_3 represent stretching modes and v_2 is a bending mode (degenerate for linear molecules) *. In triatomics with more than one minimum, it is the v_2 bending coordinate which is largely responsible for linking the minima. Several triatomics have been studied in the intermediate/high-energy region. In particular, Lehmann et al. [2] recorded the spectrum of HCN in the range 15000–18500 cm^{-1} in an attempt to observe chaos. All the levels they saw could be assigned and well fitted by standard techniques for localized states. They were thus unable to identify any chaotic states in this region, despite classical calculations which predicted chaos above 12990 cm^{-1}. We note, however, that they failed to find any state with two or more quanta in the v_2 bending mode and that in the energy range studied one would expect the bending coordinate to become delocalized [3].

Similarly, Imre et al. [4] measured the vibrational spectrum of O_3 to within 500 cm^{-1} of dissociation. Their results have been successfully fitted using both Darling–Dennison [5] and algebraic approach [6] hamiltonians, and all observed states classified as regular. However, Imre et al. [4] observed no states involving bending excitation. Classical trajectory calculations on O_3 by Farantos and Murrell [7] found chaotic trajectories 5000 cm^{-1} below dissociation. Although the experience of Lehmann et al. [8] shows that such comparisons

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* This is not so for D_{3h} molecules such as H_3^+.

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must be made with caution, the two results would appear anomalous.

Recently we have analysed the vibrational motions of KCN and LiCN using both quantum and classical mechanics [9,10]. In that work, vibrational states were characterised as regular or irregular according to the nodal patterns of their wavefunctions, the avoided crossings and second differences in the energy levels, the distribution of level spacings and the occurrence of dominant coefficients. For the classical trajectories, we computed the power spectra of the momenta, Poincaré surfaces of section, plots of the trajectories on the coordinate plane, and the rate of exponential divergence of two initially adjacent trajectories. We predicted that for both molecules an early onset of vibrational chaos is to be expected. The strong coupling between the bending and stretching modes in KCN meant that we found no quasiperiodic trajectories (although KAM theorem predicts that some must exist) or regular (localized) states embedded in the chaotic region. Conversely, in LiCN which displays weaker coupling, trajectories or quantum states with regular motion persisted over the entire energy range studied.

In this paper we further analyse the vibrational motions of LiCN. Particular attention is paid to the stretching versus bending energy distribution of the quasiperiodic trajectories and regular states embedded in the chaotic region. We show that in LiCN the onset of chaos is correlated with the degree of bending excitation and hence that regular states with a high degree of stretching excitation but little or no bending excitation can be expected to persist well into the chaotic region and possibly to dissociation (depending on the degree of coupling). This allows us to reinterpret the apparent conflict between the classical trajectory calculations and the observed highly excited vibrational states of HCN and O_3.

2. Results

The numerical methods used here to analyse the classical and quantum-mechanical motion of LiCN have been described in previous publications [9,10]. The potential energy surface used is the ab initio surface of Essers et al. [11]. This potential is a function of two variables, the distance of the Li^+ from the CN^- centre of mass, R, and the angle θ between R and the CN^- bond, r. It reproduces the observed geometry and vibrational fundamentals of LiNC($\theta = 180°$) [12] as well as predicting a local LiCN($\theta = 0°$) minimum.

We analysed trajectories with different energy partitioning between the stretch (R) and bend (θ) coordinates. To do this trajectories were started at the equilibrium geometry of LiNC (or LiCN). The energy in each mode was defined as the kinetic energy of that mode at $t = 0$. Whilst altering the initial phase of a trajectory can change in its behaviour, we do not believe the conclusions drawn below are sensitive to the phase of individual trajectories. Each trajectory was integrated for ≈ 10 ps.

Fig. 1 shows two typical trajectories with total energies of 3712 and 3394 cm^{-1} which are above the barrier to isomerisation of 3377 cm^{-1}. The quasiperiodic trajectory started with most of its energy in the stretching mode whereas the chaotic trajectory had most in the bending coordinate. We found that this behaviour was typical of trajectories above the critical energy for the transition to chaos (at ≈ 1600 cm^{-1} [10]).

The unshaded areas of fig. 2a show the range of energies in the bending and stretching modes where the trajectories were assigned as quasiperiodic. We found quasiperiodic trajectories well above the barrier to isomerisation provided only a small amount of energy was placed in the bending mode. On the other hand, all trajectories with energy more than 1500 cm^{-1} in the bending mode and zero-point energy in the stretching mode were found to be chaotic. The singly crossed region in fig. 2a separates the quasiperiodic from the chaotic (shaded) domains. This domain encompasses trajectories which were difficult to assign with a finite-time calculation.

A similar analysis has been carried out for the quantum mechanical status of LiNC (fig. 2b). The states have been assigned as regular or chaotic according to our previous criteria [10], largely by analysing their nodal structure. For quantum states it is not possible to make a rigorous decomposition of the energy into stretching and bending contri-

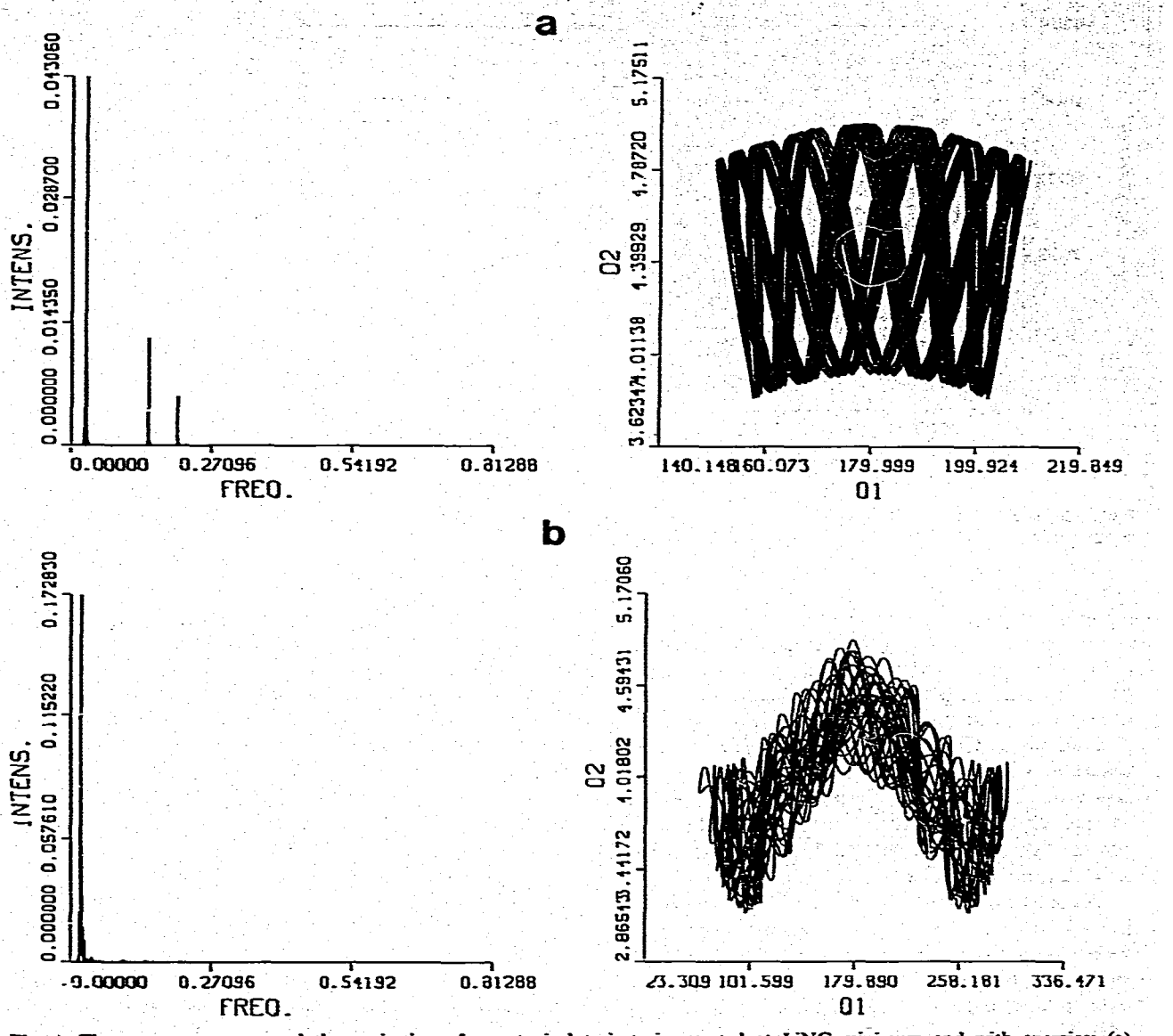


Fig. 1. The power spectrum and the projection of two typical trajectories started at LiNC minimum and with energies: (a) $E_{\text{stretch}} = 3395\ \text{cm}^{-1}$, $E_{\text{bend}} = 317\ \text{cm}^{-1}$. (b) $E_{\text{stretch}} = 377\ \text{cm}^{-1}$, $E_{\text{bend}} = 3017\ \text{cm}^{-1}$. Q_1 and Q_2 denote the bending coordinate in degrees and stretching coordinate in a_0, respectively.

butions. However, for regular states an approximate decomposition was achieved. This was done by assigning the stretching fundamental and overtones, v_1 and then writing

$$E_{\text{stretch}}(v_1, v_2) = E_{\text{total}}(v_1, 0),$$
$$E_{\text{bend}}(v_1, v_2) = E_{\text{total}}(v_1, v_2) - E_{\text{stretch}}(v_1, 0). \quad (1)$$

Other sensible definitions of E_{stretch} and E_{bend} make

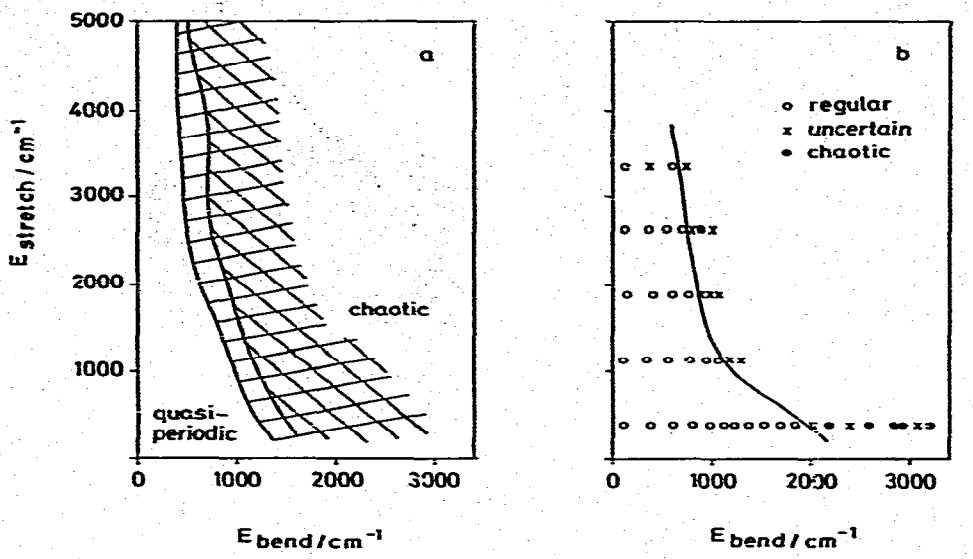


Fig. 2. Quasiperiodic–chaotic domains in LiNC as a function of bending–stretching energy. (a) Classical results for fifty trajectories. (b) Quantum results. Energies are relative to LiNC minimum.

no qualitative difference to fig. 2b.

In fig. 2b the open circles mark the regular states and crosses denote those which were difficult to designate as chaotic or regular. Closed circles represent chaotic states, for the majority of chaotic states no method of partitioning the energy could be found as not even approximate (v_1, v_2)'s could be assigned. The chaotic states not included in fig. 2b should lie to the upper right of the figure. Typical nodal pattern for regular, uncertain and chaotic states are shown in fig. 3.

States localised in the LiCN minimum have also been observed [10,12]. By assigning approximate bending and stretching quantum numbers to these states we found that regularity is again associated with a low degree of bending excitation. Fig. 4 shows a classical and quantum analysis of bend/stretch excitation in LiCN. In some regions uncertain/chaotic LiCN states were observed outside the classically chaotic domain. This is due to tunneling.

In the light of these results we have reexamined the classical trajectory results for O_3 [7] obtained using the potential energy surface of Murrell and Farantos [13]. We have examined several trajectories distributing the energy between the bending and two stretching modes. We found that exciting the symmetric stretch while keeping the bending and asymmetric stretch at their zero-point energies gave regular (localized inside the energetically available coordinate space) trajectories for total energies up to 6000 cm^{-1} (fig. 5a). This energy is measured from the minimum of the potential which is 8800 cm^{-1} below dissociation. The critical energy for the transition to chaotic has been located at ≈ 3000 cm^{-1} above the minimum [7]. Regular trajectories were also observed by exciting the asymmetric stretch for total energies up to 5000 cm^{-1}.

Combinations obtained by exciting both stretching modes by one or two quanta also resulted in localized trajectories. On the other hand, excitation of the bending mode at these energies gives chaotic behaviour (fig. 5b). Our results thus confirm the conclusions drawn for LiNC/LiCN that excitation of the stretching modes results in quasiperiodic trajectories whereas excitation of the bending mode is associated with chaotic behaviour.

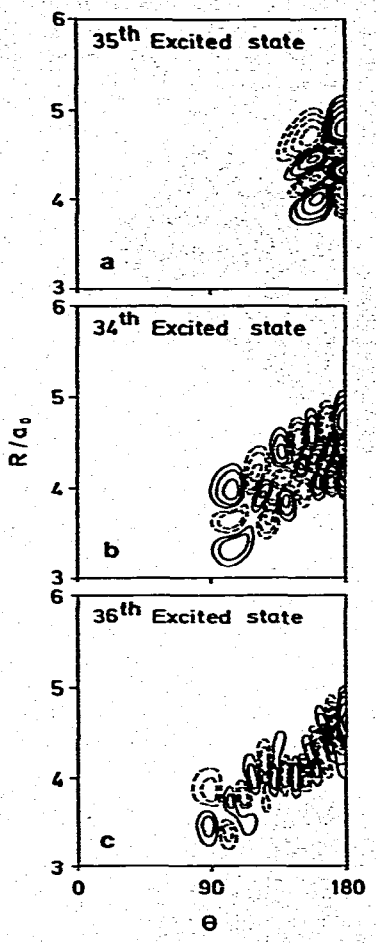
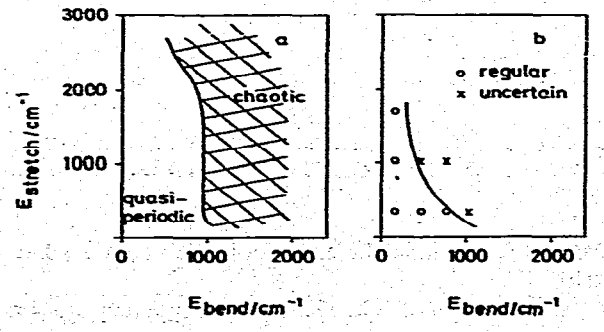


Fig. 3. Three typical vibrational wavefunctions. The contours link points where the wavefunction has 4%, 8%, 16%, 32% and 64% of its maximum amplitude. Solid curves denote positive amplitude and dashed lines negative amplitude. (a) Regular (3, 2), (b) uncertain (2, 12)?, and (c) chaotic state.



3. Discussion

The above results illustrate the importance of the bending mode in reaching the chaotic regions of phase space for a triatomic molecule. On the other hand, highly excited stretching states with little bending excitation show a regular behaviour. Although the role of mode coupling cannot be ignored, we believe this is due to the increased anharmonicity and reduced vibrational spacing in the region of a potential barrier between two minima. In triatomics this effect dominates terms in the potential associated with the bending rather than stretching coordinates. This supports Hose and Taylor's thesis [1] that extreme differences in mode motions will result in regular behaviour. However, our results suggest that this thesis is only valid, in triatomics with low barriers, for extreme stretching modes.

In accordance with ref. [1], we argue that polyatomic molecules will show non-ergodic behaviour if they are excited in states with extreme mode motions. For example, argon clusters attached to excited chemically interesting species [14–15] show highly non-statistical unimolecular dissociation properties. No fragmentation of argon clusters can be observed despite an energy excess in the chemical species of two orders of magnitude [15]. Of course, such systems are expected to show extreme mode motion.

However, for systems with more than two degrees of freedom ($N > 2$), it is not necessary for regularity to be associated with quasiperiodic trajectories. There may be only M constants of motion where $1 < M < N$. Numerical studies on three-dimensional systems have shown that trajectories with $M = 2$ can be found [16]. In this case the chaotic region of phase space is divided into different ergodic components according to the constants of motion.

Highly excited regular states have been observed in HCN [2] and O_3 [4]. However it is noticeable that all $J = 0$ states observed have the bending mode in its ground state. Analysis of our

Fig. 4. As fig. 2 but for LiCN. Total energies are relative to LiCN minimum.

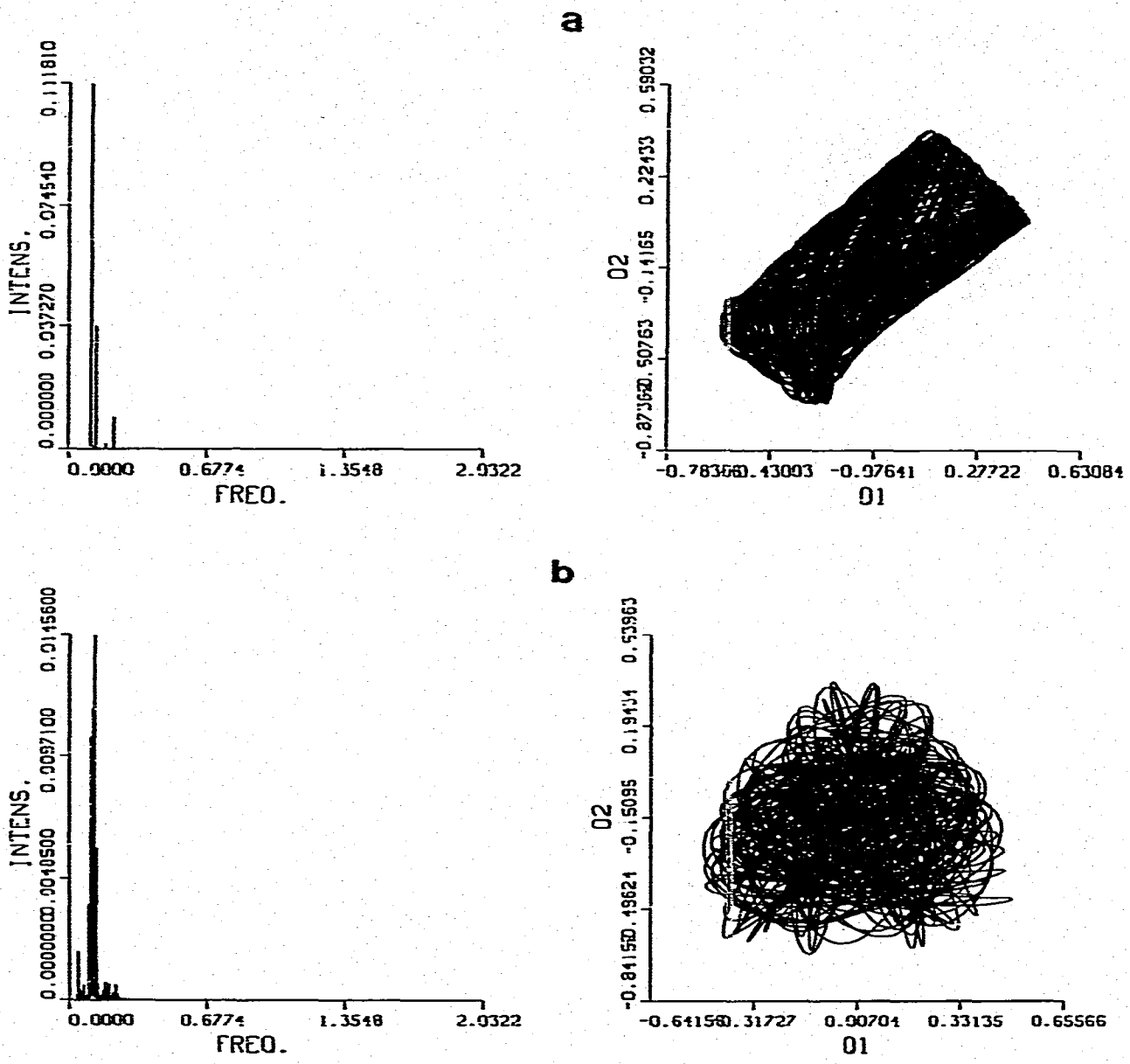


Fig. 5. The power spectrum and the projection of two typical trajectories started at O_3 minimum and with energies; (a) $E_{zz} = 397$ cm^{-1}, $E_b = 358$ cm^{-1}, $E_{ss} = 545$ cm^{-1}. (b) $E_{zz} = 568$ cm^{-1}, $E_b = 3938$ cm^{-1}, $E_{ss} = 545$ cm^{-1}. Q_1 and Q_2 denote the asymmetric and symmetric stretches respectively.

results for LiCN and O_3 suggests that the excited bending states in the region sampled are chaotic. These chaotic states would appear to have low intensity, because the transition dipoles are small [17].

Lehmann et al.'s [2,8] classical trajectory studies

on HCN using different potential energy surfaces demonstrate the sensitivity of the onset of chaos to the potential. They studied the extreme motion of the H–CN stretch and found that the onset of chaos varied by a factor of three with the potential function used. We would expect the bending mode in HCN to show chaotic behaviour in the region of the HCN/HNC barrier. Lehmann et al.'s [8] calculations thus reflect the variation in barrier height in the potentials used and the strength of the resulting mode coupling. We note that none of the potentials used were fitted to spectroscopic data in the high-energy region.

In O_3 we observe mode localized (regular) stretches well into the chaotic region; these correspond with the stretching states which have been observed almost to dissociation. Although quantum "sluggishness" [9,10] cannot be ruled out, we feel that the earlier onset of chaos in the classical trajectory results is due not to failure of classical mechanics but to the inadequate representation of mode coupling at high energies by the potential function. Comparison of our calculation on floppy molecules [9,10] shows a qualitative agreement between classical and quantum mechanics. In particular the strength of mode coupling by a given potential is reflected by both mechanics [10].

4. Conclusion

It has been shown for LiNC, LiCN and O_3 that excitation of the bending motion is the primary route to chaos. This conclusion is supported for LiNC/LiCN by both quantum and classical calculations. It is our conjecture that for most triatomics, especially those with more than one minimum or barrier in the potential, bending excitation will lead to chaos at lower total energy than by excitation of a stretching mode. Exceptions to this will be molecules, such as KCN [9,10], where strong mode coupling causes a near uniform onset of chaos.

The importance of the coupling between bending and stretching modes at intermediate and high energy means that one-dimensional hamiltonians which have been used to describe the vibrations of non-rigid triatomics (e.g. refs. [3,18]) should be used with caution. There is a remarkable difference between one-dimensional approximations where the motion is always regular and two- or three-dimensional calculations for which chaos is possible. In this context, the use of coupled stretching functions such as Morse oscillators [8,19], whilst mathematically interesting, does not provide a good model of vibrational chaos in triatomics which we believe to be strongly associated with the bending motion.

There is also a need for realistic potentials for the interpretation of vibrational spectra. Many potential energy surfaces are produced by fitting experimental data which describe a limited region of nuclear configuration space. The remaining space is then described by extrapolating the functions into the unknown regions. Our analysis of the O_3 and HCN problems suggests that accurate potential functions should reproduce mode-coupling behaviour as a function of energy. This is undoubtedly a difficult task.

We speculate that the difficulty in observing highly excited bending states for HCN and O_3 is associated with the chaotic character of these states. We feel that these bending states, and perhaps the bends in floppy molecules which have an early onset of chaos, provide good candidates for experimental investigation of chaos [20].

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