Transition intensities for the excitation of ground state LiCN to many vibrational levels, including ones previously predicted to be chaotic, are calculated. This direct excitation is found to be efficient for stretching excitations but unlikely to be useful for populating chaotic states as they require significant bending excitation. The fluorescence lifetimes for these vibrationally excited states are computed and show a remarkable structure. The regular states all lie in progressions labelled by a single stretching quantum number while the lifetimes of chaotic levels show no structure. Fluorescence spectra are found to be sharp for regular and diffuse for chaotic states. It is thus suggested that fluorescence properties could provide a useful experimental probe in the search for chaotic vibrational states.

1. Introduction

Much recent research has centred on the possibility that the highly excited vibrational states of polyatomic molecules will cease to show regular spectra with well-defined quantum numbers and become in some sense irregular or chaotic [1]. While a precise definition of what is meant by chaos in a quantum-mechanical system is still awaited, several characteristics of such systems have allowed progress to be made in identifying molecules with chaotic vibrational states. These characteristics include complicated nodal structures [2], level spacing distributions similar to that found from diagonalising random matrices [3] and instability with respect to small perturbations [4].

There have also been some claimed sightings of chaos. They include the highly excited vibrational levels of acetylene [5], high-lying rotational levels of formaldehyde [6] and vibronic states in NO2 [7]. There is still limited empirical experience in this area. Theoreticians, however, have concerned themselves largely with the calculation of energy levels and corresponding wavefunctions and, apart from some work on multiphoton processes [8], have largely ignored the role played by transition strengths in any experiment.

Two-dimensional calculations by Farantos and Tennyson [9–11] using both classical and quantum mechanics have shown that the floppy KCN and LiCN molecules, with CN frozen, display an early onset of vibrational chaos. KCN shows a particularly early onset to chaos, with only the
three lowest vibrational levels being definitively assigned as regular [9]. Previous analysis of the transition intensities for the lowest ten vibrational states of KCN showed a complicated spectrum caused by large amounts of "intensity stealing" between nearby states in resonance [12]. The occurrence of overlapping resonances is a characteristic of chaos [4]. KCN, however, is an atypical molecule as the strong coupling between the modes destroys all regularity in both the classical and quantum spectrum above the onset of chaos. This is contrary to the behaviour of more usual KAM-like systems for which regular and irregular trajectories/states exist together over a range of energies [13].

Despite its large amplitude bending mode, LiCN is probably more typical of small molecules. Its comparatively weak mode coupling leads, in keeping with KAM theory, to only the gradual destruction of stable regular orbits. Analysis has shown that the stretching motion is particularly stable and the onset of chaos is caused by bending excitation [11]. This can be rationalised in terms of the LiCN potential which shows two low-lying minima with linear geometries: LiNC (absolute) and LiCN (metastable) [14]. The bending motion links these minima and thus feels the full anharmonicity of the barrier between them, which lies at 3177 cm\(^{-1}\) above LiNC.

A dipole surface has been calculated for LiCN and some analysis of its predicted spectrum performed [12]. However, this analysis was confined largely to states lying in the lower and thus regular region of the spectrum. Fluorescence lifetimes were also computed, but only for the isomerisation process LiCN \(\rightarrow\) LiNC. In this paper we extend the analysis of transition dipole dependent properties of LiCN to consider spectra encompassing both regular and chaotic states. We compute transition intensities, which are the key to observing any of the transitions of which we are interested, and fluorescence lifetimes and spectra which recent analysis has shown to be important for understanding chaos in the observed levels of NO\(_2\) [7].

2. Transition intensities

Our calculations of the LiCN transition intensities follow closely those of Brockets et al. (BTA) [12]. Their dipole surface, \(\mu(r_e, R, \theta)\) is expressed in the body-fixed coordinates \(R\), the separation of Li from the \(^{12}\)C\(^{14}\)N centre of mass, \(r\) the CN bond length and \(\theta\) the angle between \(r\) and \(R\). The CN coordinate was frozen, as previously [10–12,14,15] at \(r_e = 2.186\ \text{a}_0\), reducing the vibrational problem to a two-dimensional one with stretching coordinate \(R\) and bending coordinate \(\theta\). BTA's fit to the ab initio dipoles of Essers et al. [14] divides the dipole components into short- and long-range contributions. Although the short-range contribution is necessary for an accurate representation of the calculated dipoles, the gross features of the surface are given by the long-range properties. In particular, the charge separation between Li\(^+\) and CN\(^-\) gives the largest contribution to the dipole. This lies along the the vector \(R\) which is chosen as the body-fixed z axis.

As we are interested in higher vibrational states than BTA, is was necessary to improve on the vibrational calculations they used. This was done using the method of Brocks and Tennyson [15], in contrast to the previous analysis of vibrational

<table>
<thead>
<tr>
<th>Excited state</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>79</th>
</tr>
</thead>
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<td>ref. [10] (^a)</td>
<td>1245.30</td>
<td>1874.83</td>
<td>2286.79</td>
<td>2669.79</td>
<td>2954.94</td>
<td>3223.41</td>
<td>3474.81</td>
<td>3655.34</td>
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<tr>
<td>this work (^b)</td>
<td>1245.28</td>
<td>1874.79</td>
<td>2286.80</td>
<td>2669.34</td>
<td>2954.64</td>
<td>3223.45</td>
<td>3474.88</td>
<td>3660.98</td>
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\(^a\) Method of Tennyson and Sutcliffe [16,17], \(n \leq 19, l \leq 44\).

\(^b\) Method of Brocks and Tennyson [15], \(n \leq 15, l \leq 44, \theta_l = 70^\circ\).
chaos in LiCN [10,11] which used the method of Tennyson and Sutcliffe [16,17]. The essential difference between these methods, which both use associated Legendre polynomials to carry the θ bending coordinate, is in the treatment of the R stretching coordinate. Brocks and Tennyson used numerical functions for R, obtained by solving a model problem defined by a cut through the potential for some fixed θ = θf. The method of Tennyson and Sutcliffe uses associated Laguerre polynomial basis functions to give Morse oscillator-like functions for R.

Table 1 compares the current band origins with those used previously. Very good agreement is obtained for the lowest 70 levels. We note that in this work we only used 16 (n ≤ 15) radial functions compared to the 20 (n ≤ 19) required by Farantos and Tennyson [10] to obtain roughly the same accuracy.

For a molecule like LiCN, with large vibrational spacings, only a few low-lying vibrational levels will be thermally occupied. Excitation, within the ground electronic state, to chaotic regions of the spectrum will thus usually involve many quanta of vibrational excitation. This excitation could be driven either by a multiphoton process, which may be efficient at climbing ladders of regularity [8] but is less likely to be an efficient probe of the irregular regions, or by a single, high-intensity jump. The ladder method was used by Lehmann et al. to probe HCN [18] in an unsuccessful attempt to identify chaotic states.

The absorption coefficient for an electronic dipole transition from state m to state n (m and n non-degenerate) is given by the golden rule expression

\[ K(ω) = \left( \frac{4π^2}{3hc} \right)ω\delta(ω - ω_{mn})(N_m - N_n) \times \sum_j |\langle ψ_m | μ_j | ψ_n⟩|^2, \]  

where \( N_i \) is the density of molecules in state i and ω_{mn} is the frequency of the transition. The summation over components of the transition dipole operator is usually known as the transition line strength.

Fig. 1 shows transition line strengths for transitions from the LiNC ground state below 3400 cm⁻¹. The figure has been divided to show transitions with approximate Δk = 0 and 1 separately. k, the projection of J on the body-fixed z axis (R), is only a good quantum number when certain Coriolis interactions are neglected [15,16]. However, for LiCN it is an approximately good quantum number [12,15] and the analysis is greatly eased by making this labelling.

Calculations which include the full Coriolis coupling for the J = 1 state gave only minor shifts in the energy levels, because of the slight mixing between k = 0 and 1 states. This is not so for the transition intensities. For the pure states, the k = 0 → 1 intensities depend on \( μ_z \), and the Δk = 0 intensities on \( μ_x \). As \( μ_z \) is dominated by the charge separation it is much larger than \( μ_x \), leading to pure Δk = 0 transitions of much greater intensity than the Δk = 1 ones. However, even a small perturbation of the pure k levels leads to a major enhancement of the Δk = 1 line strengths. Therefore, although we will make use of k as an approximate quantum number, all calculations presented here include full Coriolis coupling.

In fig. 1 the excited vibrational states have been assigned as regular and localised about LiNC or LiCN, chaotic or unclear. These assignments were made independently for J = 1, k ≈ 0 states, which followed the J = 0, k = 0 assignments made previously [11], and for the J = 1, k ≈ 1 levels. The assignments were made principally by inspection of the nodal structure of the wavefunctions, unclear states whose regular nodal structure had been partially destroyed by mixing, but for which approximate quantum numbers could be assigned by assuming an idealised nodal structure. Further details can be found in ref. [11].

There are several features of note in fig. 1. Firstly, the most intense transitions involve excitation of the stretching coordinate because of the large dependence of the dipole on the value of R. Thus the four transitions whose intensities lie in a line on the left-hand side of the figure correspond to the stretching fundamental and its lowest three overtones. A similar progression can be seen for the bending overtones on the lower right-hand side of the figure, although this progression is less regular.

For high-frequency transitions these progressions, particularly the bending one, merge into a region of low-intensity transitions with little struc-
Fig. 1. Line strengths for direct excitation of the ground vibrational state of LiCN versus transition frequency (a) \((J, k) = (0, 0) \to (1, 0)\) and (b) \((J, k) = (0, 0) \to (1, 1)\). Each point is labelled according to the nature of the excited state; see text for details.
ture. The majority of the transitions in this region lead to chaotic states, the exceptions being transitions which involve isomerisation. Franck–Condon overlap considerations show that such photon-driven isomerisation will have extremely low intensity.

3. Fluorescence

A molecule in a vibrationally excited state has a finite probability per unit time of spontaneously emitting a photon and going to a state of lower vibrational excitation. The coefficient of spontaneous radiative decay of non-degenerate state \( m \) into non-degenerate state \( n \) is given by

\[
A_{mn} = \left(4\omega_{mn}^2/3\hbar c\right) \sum_j |\langle \psi_m | \mu_j | \psi_n \rangle|^2. \tag{2}
\]

This can be converted into a fluorescence lifetime by summing over all the states into which state \( m \) can decay:

\[
\tau_m = \left( \sum_n A_{mn} \right)^{-1}. \tag{3}
\]

This will be the lifetime of such a state in a collision-free environment.

Fig. 2 shows fluorescence lifetimes for vibrationally excited states of LiNC lying less than 3400 cm\(^{-1}\) above the ground state. Regular states localised at the LiCN minimum have been excluded from the figure as they have very long lifetimes. These lifetimes were calculated by considering all allowed transitions from the vibrational state with \( J = 0 \) to vibrational states with \( J = 1 \). Full Coriolis coupling was included in the calculation of the wavefunctions of the \( J = 1 \) states as its neglect was found to significantly alter the fluorescence lifetimes in some cases.

Fig. 2 shows that all the regular excited states lie in five progressions. Analysis of the states involved showed that for each progression all states have the same degree of stretching excitation \( (v_s) \), the quantum numbers of neighbouring points differing only by two quanta of bending excitation \( (v_b) \). Note that as LiNC is a linear molecule the \( J = 0 \) bending states all have \( v_b \) even. The progression with the longest fluorescence lifetimes has no stretching excitation \( v_s = 0 \), the next has \( v_s = 1 \), etc.
For states lying more than 2000 cm\(^{-1}\) above the ground vibrational state there is a group of states with lifetimes in the range 0.04–0.2 s which show little or no structure. These states can be, at best, assigned tentative quantum numbers and are thus labelled either unclear or chaotic. All the progressions with good numbers appear to lead towards this region, reaching it at a point where assignment of quantum numbers ceases to be possible.

The fluorescence lifetime of an excited state is not the only characteristic that can in principle be observed. Each excited state also has a characteristic spectrum associated with its fluorescence. We have studied the fluorescence spectrum of several vibrationally excited states of LiNC in the energy region above the transition to chaos where both regular and chaotic states can be found.

Fig. 3 shows typical fluorescence spectra belonging to a regular, an unclear and a chaotic state. The spectra are ordered to show increasing complexity. So while the spectrum \(\nu\) of the (4,0) state is dominated by one single transition, to the (3,0) state, many transitions make a significant contribution to the decomposition of the chaotic state, fig. 3c.

\(\nu\) denotes the stretching and bending vibrational quantum numbers.

4. Discussion

It is clear from the vibrational transition intensities of fig. 1 that the direct excitation of any of the chaotic states from the ground state is very improbable. These transitions from the ground state are all more than 10 orders of magnitude less intense than excitation of the stretching fundamental. This is in contrast to excitation of the regular (4,0) state, which is well above the onset of chaos and is only \(10^6\) weaker than the stretching fundamental.

This behaviour is not so much a reflection of the chaotic behaviour of LiCN but the greater intensity of stretching excitations because of the ionic nature of the molecule. Similar behaviour was found in HCN by Lehmann et al. [18] who were able to probe a large number of stretching states by direct excitation of the ground state. However, they resolved virtually no bending excitations. As these bending states are likely to play a crucial role in the onset of chaos [11], their search for irregular states was thus unsuccessful.

However, there are other viable routes to the preparation of a molecule in highly excited vibrational states of the electronic state. A particularly promising method involves pumping to a suitable level in an electronically excited state and then either allowing this level to fluoresce or encouraging it to undergo stimulated emission back to the ground electronic state. If there are significant differences in the geometry of the two electronic states involved, then many vibrational levels of the electronic ground states can be populated.

Electronically excited states have been used as a probe for large numbers of ground vibrational levels in molecules such as acetylene, formaldehyde and HCP. In acetylene [5] and formaldehyde [6] chaotic levels were identified, while HCP showed remarkable regularity even with up to 27 quanta of bending excitation [19].

For certain weakly bound molecules, it is possible that irregular regions of the spectrum may be occupied thermally. Calculations on the Ar HCl molecule [20] indicate that van der Waals complexes may have chaotic states which are likely to be occupied at experimental temperatures.

Besides the qualitative feature that transitions
to regular LiNC states are more intense than transitions to chaotic states, fig. 1 also shows some structure. The line strengths of the stretching overtone transitions lie on a near straight line and a similar progression can also be seen for the bending overtones. Some correlation can also be made for regular states with both bending and stretching excitation. No structure, apart from the ultra-low intensity transitions to the LiCN discussed above, can be seen in the low intensity, largely chaotic portion of fig. 1.

The fluorescence lifetimes of the regular states depicted in fig. 2 show an even more pronounced structure than fig. 1. All the regular states lie on progressions which can each be labelled by a single stretching quantum number. All the chaotic states lie in a clump separated from these progressions. Many of the unclear states, for which approximate quantum numbers could be assigned, appear to link the regular progressions with the chaotic clump.

Another interesting feature of fig. 2 is that the progression with \( \nu_s = 0 \) shows a large decrease in lifetime with bending excitation, while the progressions with \( \nu_s > 0 \) show a small increase. This can be understood in terms of the dominant role played by the stretching mode in the fluorescence lifetimes. As the bending excitation increases, so does mode mixing. This mode mixing introduces some stretching character into the “pure” bending states leading to a sharp decrease in lifetimes. Conversely, the mode mixing on the \( \nu_s > 0 \) states leads to some bending character being introduced into the stretching states and a consequent slight increase in lifetime. In the chaotic region mode mixing is complete and no distinction can be made between states with predominantly bending or stretching character. All the fluorescence lif-

Fig. 4. Fraction of the fluorescent decay intensity carried by the dominant transition versus excitation energy for the low-lying states of LiNC with \( J = 0 \). Designations are (O) LiNC regular, (A) unclear and (●) chaotic.
times are thus the same within some statistical fluctuation.

The simulated fluorescence spectra, fig. 3, also show a markedly different behaviour between regular and chaotic states. The decay of regular states is dominated by a few transitions, that with \( \Delta v = -1 \) being the most important when \( v > 0 \). Conversely, the relaxation of the usual vibrational selection rules for chaotic states results in many transitions with significant intensity. This situation is reminiscent of the power spectrum of a classical trajectory which is simple and discrete for a quasiperiodic trajectory and shows structure for chaotic trajectories [21].

Fig. 4 gives a more quantitative representation, for all the low-lying states, of the trends shown in fig. 3. Fig. 4 displays the fraction of the total fluorescence intensity which is carried by the dominant (most intense) transition for each state. As one would expect, for most regular states decay is via one dominant transition whereas for all the states designated chaotic, no more than 63% of the intensity is carried by the dominant transition. The progressions observed in fig. 2 are also apparent in fig. 4, with the stretching overtone states being those most dominated, 95%, by a single transition.

5. Conclusions

It is well known that for many model and real systems, regular (mode localised) and irregular (mode delocalised) states can be found in classically chaotic energy regions [22]. Analysis of triatomic molecules [11], where the separation between states is large, and polyatomic systems [23], whose states form a quasi-continuum, has shown that regularity (mode localisation) can be associated with stretching overtones. LiCN is no exception to this. In the light of this we have analysed the dipole-dependent properties of LiCN using realistic, ab initio potential energy and dipole surfaces in a computer experiment.

Our calculations on the LiCN molecule suggest that direct vibrational excitation of the ground state is not likely to be a useful technique for reaching chaotic regions of the spectrum. However, alternative experimental methods using an initial vibronic transition show more promise for reaching this goal.

While the transition intensities do show some structure, this is much more spectacular for the fluorescence lifetimes which show significant changes in character for regular and chaotic states. This is similar to the conclusions drawn by Hardwick from his study of a variety of NO\textsubscript{2} vibronic data [7]. Besides the fluorescence lifetimes, the fluorescence spectra also appear to contain characteristic information concerning the regular/chaotic nature of the fluorescing state. The breakdown in the vibrational selection rules, or more correctly propensities, is clearly shown by the increased number of transitions with significant intensity from the chaotic states. It is hoped that the analysis of fluorescence behaviour might be as useful for the empirical identification of chaos in vibrational manifolds as it already has been in the vibronic manifold of NO\textsubscript{2} [7]. Finally we note that time- and frequency-resolved fluorescence spectra have provided useful information for analysing intramolecular vibrational redistribution in polyatomic molecules [24] which is driven by mode coupling similar to that found in chaotic states.

References