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Quantum vibrational chaos in the ArHCl van der Waals molecule

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Quantum mechanical ro-vibrational calculations are presented for the ArHCl van der Waals complex using Hutson and Howard's empirical M5 potential. Analysis of the nodal structures, second differences and overlapping avoided crossings suggests that the higher bound states of ArHCl are chaotic. This chaos is made evident by perturbing the angular part of the kinetic energy term, e.g. by isotopic substitution or vibrational excitation of HCl. Calculations with $J > 0$ show increased level crossings but no significant increase in chaos because of an extra nearly good quantum number. The low-lying states of ArHCl appear to be poorly modelled by either the harmonic oscillator or free rotor approximations. Comparison with other molecules for which vibrational chaos has been predicted are made.

1. INTRODUCTION

In a recent series of papers [1–3] Tennyson and Farantos studied the onset and nature of vibrational chaos in the floppy KCN and LiCN molecules. They did this by performing quantum and classical calculations on realistic (*ab initio*) potential energy surfaces. Quantum chaos was identified by using a variety of previously proposed criteria [4] including nodal structure [5], spectral distributions [6], second differences [7] and the occurrence of overlapping avoided crossings [8]. While no criterion was found to give a complete solution to the problem of characterising quantum chaos, the combination of indicators allowed chaos to be identified. Qualitative agreement was also obtained between classical and quantum calculations, although some quantum sluggishness was observed. The unusually early onset of chaos in both KCN and LiCN was found to be closely associated with the presence of low-lying barriers in the bending coordinate [3].

Many van der Waals complexes have low-lying barriers in their intermolecular bending coordinate(s). Furthermore there is evidence from both classical calculations [9] and experiment [10] that Ar clusters behave chaotically. As the low dissociation energy of van der Waals systems means that most or all of their vibrational levels are thermally occupied, they would appear promising candidates for the experimental study of chaos.

The simplest van der Waals complexes that could display chaos are atom–diatom systems. Complexes formed by light diatomics, especially H_2, have only small barriers in the bending coordinate. Such systems have been studied by LeRoy and co-workers [11], who were able to obtain entire anisotropic potentials for such systems by inversion of (well resolved) infra red spectra. The isotropic nature of these systems means that they are very well represented by the free rotor approximation. Indeed a model based on this approximation has been successfully used for the analysis of H_2X (X = rare gas) hyperfine spectra [12]. Vibrational calculations on H_2X van der Waals complexes using free rotor basis functions show that individual states are generally dominated by one basis function [13]—these states can thus be assigned regular (or 'mode localized') by the dominant coefficient criteria of Hose and Taylor [14].

Conversely, van der Waals complexes involving heavy diatomics show considerable anisotropy. Their infra red spectra are complicated envelopes (for example references [15, 16]) which require sophisticated averaging procedures to be reproduced theoretically [17]. Without resolving the mass of competing transitions only limited information about the potential can be obtained from these spectra. However, empirical potentials can be obtained for such systems by the study of scattering data, for example [18, 19].

The ArHCl van der Waals system is an interesting example of a complex with a strong anisotropic component. It has been much studied theoretically [17–22] due, at least in part, to the accurate empirical potentials obtained by Hutson and Howard [18, 19]. In particular, their M5 potential [19] has been used successfully for theoretical calculations [17, 22]. This potential predicts minima for both linear structures of the ArHCl complex, separated by a barrier of 76 cm^{-1}. As this is qualitatively the shape of potential which has been found to support chaos in LiCN [2, 3], the purpose of this paper is to ask whether some of the vibrational states of ArHCl are chaotic and if so how they might effect the predicted behaviour of the molecules.

2. CALCULATIONS ON $ArH^{35}Cl$

The hamiltonian for an atom–diatom complex can conveniently be written in body-fixed coordinates as [23]

$$H = \frac{-\hbar^2}{2\mu_1 R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right)\frac{-\hbar^2}{2\mu_2 r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{j^2}{2\mu_2 r^2}+\frac{(J-j)^2}{2\mu R^2}+V(R, r, \theta), \tag{1}$$

where μ_1 and μ_2 are the reduced masses, and $\mathbf{J}$ and $\mathbf{j}$ are the total angular momentum operators of the complex and diatom respectively; r is the diatomic bondlength, R the separation of the atom from the diatom centre of mass and θ the angle between $\mathbf{r}$ and $\mathbf{R}$. θ is 0° for linear ArHCl and 180° for ArClH. The M5 potential, V, of Hutson and Howard [19] is only a two dimensional function of R and θ. Following other workers [17, 20–22], the Hamiltonian (1) was initially solved with r frozen at the equilibrium value of $2{\cdot}435\,a_0$.

Variational solutions of (1) were obtained using program ATOMDIAT [24] with the GENPOT addendum [25]. This method, due to Tennyson and Sutcliffe [26], uses a basis expansion of Morse-like oscillators for R and associated Legendre functions (free rotor functions) for θ. Trial calculations showed that 21 Morse functions with $R_1 = 9{\cdot}8\,a_0$, $D_1 = 0{\cdot}0004\,E_h$ and $\omega_1 = 5 \times 10^{-4} E_h$ and 12 Legendre functions (for $J = 0$) converged 15 bound states for $ArH^{35}Cl$ to within $0{\cdot}05\,\mathrm{cm}^{-1}$ for the highest states and considerably better for the lower ones. Whilst the existence of further bound states cannot be ruled out on the basis of a

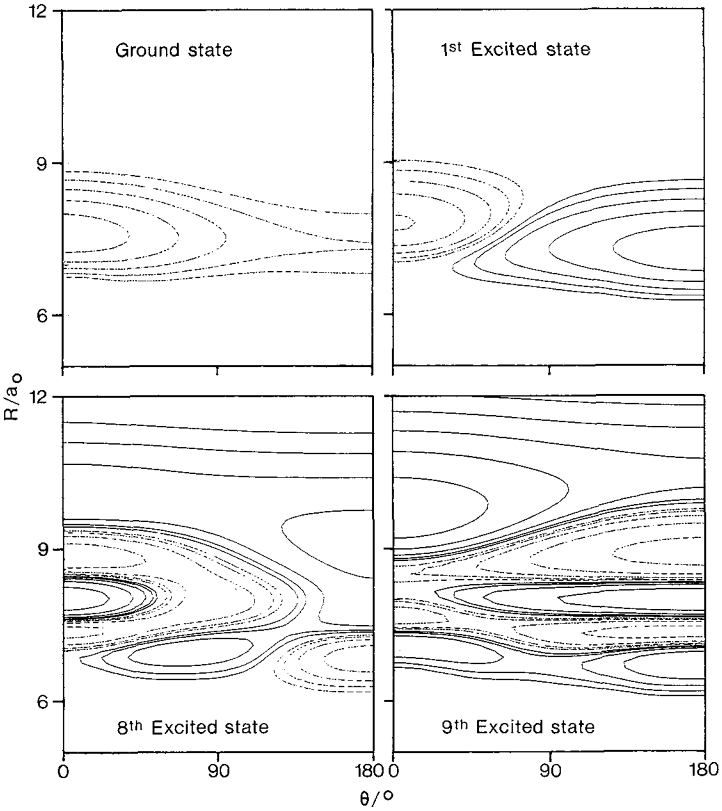

Figure 1. Amplitudes of 4 vibrational states of $ArH^{35}Cl$ with $J = 0$. The contours link points where the wavefunction has 4%, 8%, 16%, 32% and 64% of its maximum amplitude. Solid contours enclose regions of positive amplitude and negative contours regions of negative amplitude.

variational calculation, these are only likely with very low binding energy and large $\langle R \rangle$. Additional states of this type will have little effect on the conclusions drawn below.

Figure 1 shows plots of 4 typical $ArH^{35}Cl$ wavefunctions for $J = 0$ vibrational states. While the ground state shows some delocalization, it is substantially localized about the ArHCl minimum. Conversely, the first excited state, a bending excitation, is clearly delocalized. Higher excited states are characterized by complicated nodal patterns at short R and simple delocalized behaviour at large R. These states cannot meaningfully be assigned quantum numbers by inspection which is one indication of chaos [5].

The stability of levels with respect to a small perturbation is another means that has successfully been used to detect quantum chaos. Pomphrey's use of second differences [7] and Marcus *et al*'s overlapping avoided crossings [8] are based on this. In a real problem such as this, the appropriate perturbation is not readily apparent. We thus chose to study 5 perturbations which in turn affect all parts of the Hamiltonian (1). The parameters varied were m_{Ar}, the mass of Ar, and r, the HCl separation, which perturb the kinetic energy operator, and ε, $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ which between them perturb all parts of the potential [19] and are

Table 1. Second differences for five parameters (see text) for the bound states of $ArH^{35}Cl$ with $J = 0$.

Parameter	m_{Ar}	r	ε_0	$\Delta\varepsilon_1$	$\Delta\varepsilon_2$
p_0	40 amu	2·35 a_0	†	†	†
Δp	2 amu	0·05 a_0	0·025	0·02	0·04
State			Δ_i/cm^{-1}		
1	0·018	0·001	0·005	0·035	0·004
2	0·017	0·039	0·008	0·015	0·044
3	0·043	0·013	0·013	0·007	0·014
4	0·037	0·022	0·026	0·004	0·017
5	0·050	0·007	0·045	0·037	0·004
6	0·026	0·021	0·012	0·012	0·004
7	0·053	0·071	0·058	0·019	0·024
8	0·055	0·087	0·002	0·013	0·017
9	0·035	1·177	0·003	0·092	0·020
10	0·049	0·268	0·024	0·039	0·001
11	0·048	0·208	0·075	0·023	0·004
12	0·030	0·313	0·009	0·005	0·003
13	0·053	0·333	0·156	0·014	0
14	0·024	0·417	0·047	0·006	0·001

† The potential parameters, which are functions of θ, are as defined by reference [19]. They were scaled in the perturbed calculations by $(1 + \Delta p)$.

increasingly anisotropic. Table 1 shows second differences obtained for the ith state as a function of parameter p using the formula [7]

$$\Delta_i = |(E_i(p_0 + \Delta p) - E_i(p_0)) - (E_i(p_0) - E_i(p_0 - \Delta p))|. \quad (2)$$

Values of Δp were chosen so as to give second differences for the lower states of approximately the same magnitude. For one perturbation, r, the second differences shown in table 1 are significantly larger for the upper 7 states than the lower states. This is indicative of chaos [7].

Figure 2 shows the energy levels of the ArHCl problem plotted as a function of r. Inspection of the figure reveals that states bound by less than 40 cm^{-1} undergo many avoided crossings. This again indicates that these states are chaotic [8]. Conversely, plots of eigenenergy as a function of the other parameters considered in table 1 show no such erratic behaviour and imply that all states are regular with respect to these perturbations.

In general the density of states of a system increases with total angular momentum, J. This has led to suggestions that chaos will manifest itself more strongly for rotationally excited states because of the increased probability of near-resonant interactions. Figure 3 depicts the $J = 1^e$ and $J = 2^e$, where e denotes the positive parity combination [27], levels as a function of r. These figures again show many (overlapping) avoided crossings in the high energy region.

An additional indicator of chaos which has proved useful in previous calculations is the use of spectral distributions [4, 6]. This measure is based on the shape of histograms of the spacings between levels of the same symmetry. For good statistics, however, many levels are required. With less than 15 levels in the chaotic region and fewer below, even for $J = 2^e$, ArHCl supports insufficient levels to make a distributional analysis useful.

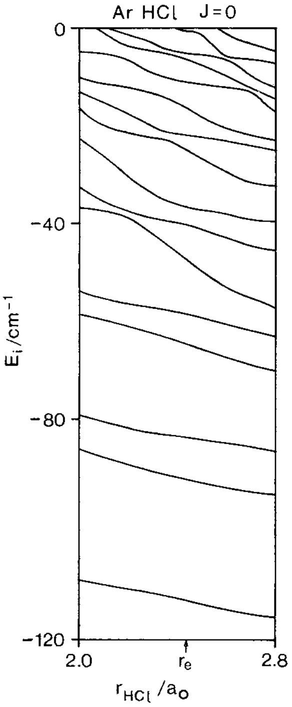

Figure 2. Vibrational energies as a function of HCl separation for $ArH^{35}Cl$ with $J = 0$.

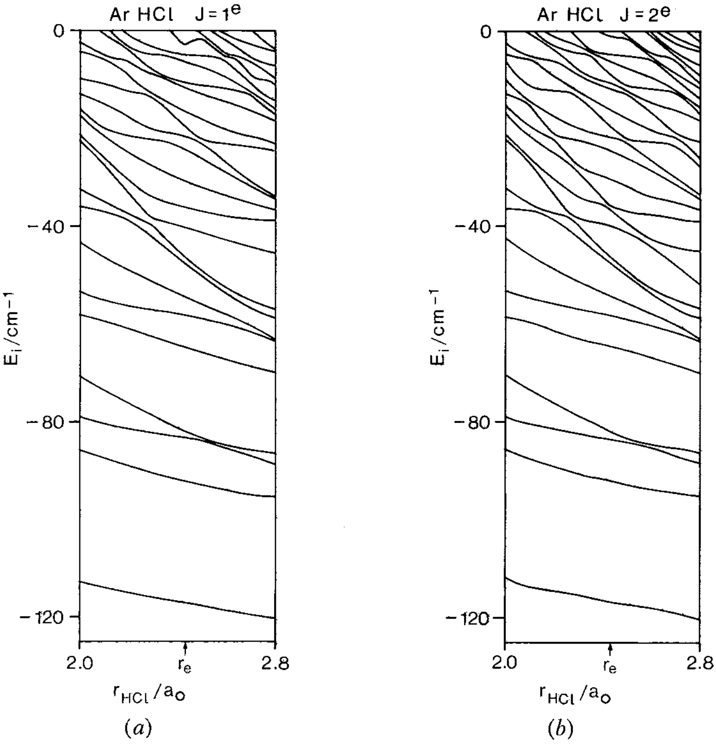

Figure 3. Vibrational energies as a function of HCl separation for $ArH^{35}Cl$ with (*a*) $J = 1^e$ and (*b*) $J = 2^e$.

3. Discussion

The calculations presented in the previous section strongly imply that the higher bound vibrational states in the M5 ArHCl potential are chaotic. Not only are these states too irregular to make the assignment of quantum numbers on the basis of their nodal structure meaningful, but also they behave erratically when perturbed by changing r, the HCl bondlength. The implication of this is that vibrational chaos in ArHCl is not induced by the potential as has been predicted for KCN [1] and LCN [2, 3] but by the kinetic energy operator. As a check on the effect of perturbing the kinetic energy operator in these systems, calculations were performed for KCN as a function of CN bondlength, r. The results are given in figure 4, which, although it shows an increasing number of avoided crossings, does not show the large number of resonances from 400 cm^{-1} above the gound state upwards, displayed when a perturbation of the potential was used [1].

Chaos is usually understood both in classical and quantum mechanics through the partitioning of a given problem into a separable (non-chaotic) zeroth order problem, H_0, which is then coupled by some chaos inducing perturbation. Indeed this concept is fundamental to both KAM theory and Hose and Taylor's 'Quantum KAM theory' [28].

In conventional (near rigid) molecules the harmonic oscillator model provides a good H_0 which usually allows many vibrational states to be assigned. For example, this model provides a good description of the lowest (regular) states in KCN [29] and LiCN [30], although in the floppy molecules it soon breaks down [1, 2, 31].

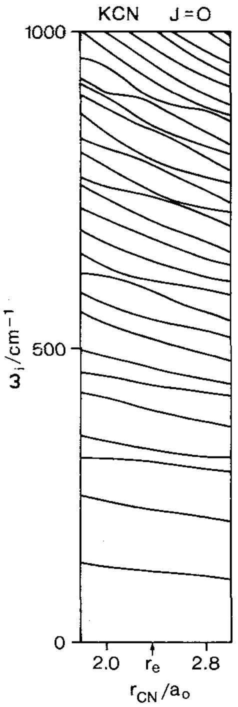

Figure 4. Vibrational energies as a function of CN separation for KCN with $J = 0$.

In atom–light diatom van der Waals dimers, such as H_2X, ($X = H$ [13], Noble gas [11, 26]) or HeHF [32], the free rotor model provides a good H_0. Work on a heavier complex, the nitrogen dimer, has shown that both the harmonic oscillator [33] and free rotor [34] models provide a poor description of the molecular vibrations, and that even the lowest states must be regarded as solutions intermediate between these models [35].

Inspection of the lowest vibrational wavefunctions of ArHCl suggests a picture similar to that found for $(N_2)_2$. The ground state is substantially localized about $\theta = 0°$, although some delocalization (and for this state tunnelling) can be observed, see figure 1. The first excited state is a single bending excitation and is delocalized. The second excited state is, largely, a single stretching excitation localized about ArHCl ($\theta = 0°$). The third excited state is a combination between a delocalized double bending excitation and a single stretching excitation localized about ArClH ($\theta = 180°$). Above these it becomes increasingly difficult to assign states by inspection. This trend appears to be uniform and suggest that ArHCl is nearer to KCN, where no regular states could be assigned or classical trajectories observed above transition to chaos [1], than LiCN where both regular states and quasiperiodic trajectories were found over the entire range studied [2, 3]. ArHCl thus appears to be strongly mode coupled.

Figure 3 shows that increasing the rotational energy of the system does indeed increase the number of levels and hence the number of avoided crossings. However, comparison of figure 2 and figure 3 gives little evidence for the lower onset of chaos in the rotationally excited systems. This is because although there are more avoided crossings in these systems, many of the crossings are only weakly avoided. This is due to the presence of a near-good quantum number, K, the projection of J along $\mathbf{R}$, which means that levels with different K only weakly interact. This behaviour is well known in van der Waals systems and has been used in approximations which neglect Coriolis interactions [20, 21, 26].

Of course the ability to perturb the ArHCl complex by choosing a value of the HCl bondlength, r, is one which is only available to the theorist. There are, however, ways in which sensitivity to r might manifest itself experimentally. Firstly, in the real ArHCl molecule, the HCl coordinate is not frozen; different vibrational states of HCl have different $\langle r \rangle$. Secondly, isotopic substitution in HCl perturbs the same terms in the Hamiltonian as changing r.

Table 2 gives energies of the vibrational levels of the ArHCl molecule relative to HCl in its ground and first excited state. For comparison the results of a calculation with HCl fixed at its equilibrium separation are also given. The r dependent calculations were performed using an empirically derived HCl potential due to Ogilvie [36]. Three Morse oscillator-like functions were used to represent this coordinate with $r_2 = 2{\cdot}465\, a_0$, $\omega_2 = 0{\cdot}012\, E_h$ and $D_2 = 0{\cdot}1045\, E_h$ [24]. This basis reproduced the observed HCl vibrational fundamental to within 0·01 per cent ($0{\cdot}2\,\text{cm}^{-1}$). No potential coupling between r and (R, θ) was allowed for.

Previous calculations on the binding energy of van der Waals dimers as a function of monomer vibrational state have been performed on the HeHF molecule [32]. This complex, which is highly isotropic, showed systematic (but small) increases in binding energy as firstly the HF coordinate was unfrozen and secondly HF vibrational excitation increased. Similar behaviour can be seen for the low-lying levels of ArHCl shown in table 2. This is due to increases in $\langle r \rangle$ with HCl vibrational relaxation and excitation. However, the 6th state of ArHCl is

Table 2. Vibrational energy levels (in cm^{-1}) relative to free Ar and H^{35}Cl(v) for ArH^{35}Cl as a function of HCl vibrational state v. Results for a fixed nuclei calculation are given for comparison.

States	Fixed†	$v = 0$	$v = 1$
1	−117·24	−117·30	−117·49
2	−92·33	−92·38	−92·61
3	−83·76	−85·80	−83·98
4	−65·04	−65·07	−65·42
5	−58·70	−58·76	−58·97
6	−47·88	−47·71	−48·85
7	−40·56	−40·58	−40·95
8	−36·60	−36·65	−36·89
9	−24·98	−24·93	−25·64
10	−22·01	−22·10	−22·19
11	−16·81	−16·73	−17·49
12	−11·09	−11·17	−11·30
13	−6·68	−6·66	−7·22
14	−5·17	−5·28	−5·27
15	−0·36	−0·43	−0·69

† $r = 2{\cdot}435\,a_0$.

actually less bound in the full calculations, this must be associated with the avoided crossing undergone by this state as r is varied, see figure 2. Above this level there is increasingly erratic behaviour with vibrational excitation. Some states become markedly more bound (e.g. numbers 9 and 11) whilst state 14 actually has a slight decrease in binding.

Table 3. Vibrational energy levels (in cm^{-1} relative to free Ar + HCl) for the major isotopic species of ArHCl with $J = 0$.

States	ArH^{35}Cl	ArH^{37}Cl	ArD^{35}Cl	ArD^{37}Cl
1	−117·24	−117·53	−125·13	−125·46
2	−92·33	−92·58	−98·64	−98·87
3	−83·76	−84·40	−91·01	−91·65
4	−65·04	−65·55	−80·08	−80·44
5	−58·70	−59·48	−69·42	−70·01
6	−47·88	−48·37	−61·74	−62·59
7	−40·56	−41·31	−55·84	−56·32
8	−36·60	−37·45	−47·15	−47·73
9	−24·98	−25·74	−44·56	−45·39
10	−22·01	−22·83	−37·31	−38·19
11	−16·81	−17·57	−33·34	−34·04
12	−11·09	−11·75	−25·44	−26·33
13	−6·68	−7·51	−24·06	−24·82
14	−5·17	−5·71	−18·77	−19·49
15	−0·36	−0·99	−15·68	−16·46
16			−12·22	−12·91
17			−8·65	−9·43
18			−5·83	−6·35
19			−3·70	−4·42
20			−1·77	−2·43
21			−0·13	−0·79

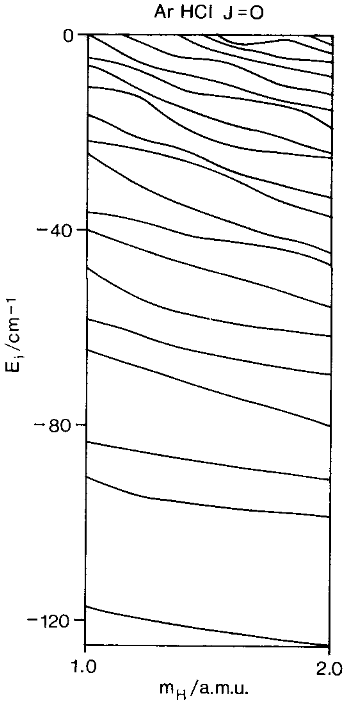

Figure 5. Vibrational energies as a function of hydrogen mass for $ArH^{35}Cl$ with $J = 0$.

This behaviour suggests that vibrational chaos in the higher states of ArHCl could be observed experimentally by studying the spectrum as a function of HCl excitation. However, the relatively small fluctuations in binding predicted will require experimental resolution well beyond that which has been achieved for these systems.

Table 3 gives the vibrational levels of the major isotopic species of the ArHCl complex. To illustrate any erratic behaviour with respect to isotopic substitution, figure 5 shows the correlation of $ArH^{35}Cl$ levels with those of $ArD^{35}Cl$ obtained by systematically increasing the mass of hydrogen. The figure is qualitatively similar to figure 2 and suggests that one would indeed expect erratic isotope shifts for the weakly bound levels of the complex. This is in contrast to calculations of KCN which indicate that the isotope shift is likely to be regular [2].

4. CONCLUSIONS

Calculations performed on the ArHCl van der Waals molecule indicate that the vibrational states which are bound by less than 40 cm^{-1} are chaotic. The transition to chaos thus occurs at about 2/3 of the way dissociation, this is similar to the figure suggested for conventional molecules, such as SO_2 [37], on the basis of classical calculations, but considerably higher than the transition in the floppy KCN and LiCN molecules [1, 2].

Chaos in ArHCl appears to be driven by the kinetic energy operator. This is in contrast to KCN and LiCN where chaos was found to be driven by the potential [1, 2]. Although model calculations have been performed on problems where chaos is caused by kinetic coupling [8], we know of no previous case where this has been predicted for a physical system.

From the point of view of experiment, this kinetically driven chaos would appear to have the advantage that there are distinct mechanisms by which chaos may be identified, namely erratic behaviour with respect to isotopic substitution and the degree of HCl excitation. However, the complexity of the ArHCl spectrum is such [17], that the resolution required to resolve such erratic behaviour may prove difficult to achieve. To this end further work is required on the occurrence of vibrational chaos in van der Waals systems, firstly to determine whether its occurrence can be predicted in any systematic way and secondly to find experimentally favourable cases for investigation.

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