New Concepts in Physical Chemistry
Ed. L.S. Cederbaum et al
(Reidel, Dordrecht, 1988)

(6?)

A RO-VIBRATIONAL STUDY OF REGULAR/IRREGULAR BEHAVIOUR OF THE CO-Ar SYSTEM

Stavros C. Farantos
Department of Chemistry, University of Crete,
and Institute of Electronic Structure and Laser,
Research Center of Crete, P.O. Box 1527
711 10 Iraklion, Crete, Greece.

and

Jonathan Tennyson
Department of Physics and Astronomy,
University College London,
Gower street, London WC1E 6BT, England.

ABSTRACT. Classical and quantum mechanical rotational - vibrational calculations have been performed for the bound states of the van der Waals system CO-Ar. From the nodal patterns of the eigenfunctions and the predominant coefficients in the basis set expansion, it is shown that the regular/irregular classical and quantum behaviour are in qualitative agreement. Regular/localized states are associated with those states which have one, two and three quanta in the bending mode but no excitation in the stretching mode. For the present system it is found that the projection of the total angular momentum on the body fixed z-axis is an almost good quantum number. Thus mixing among the zero order basis functions occur through the potential part of the hamiltonian.

1. Introduction

Non-linear mechanics has made considerable advances, during the last twenty years in understanding the regular/chaotic motion of dynamical systems [1]. This has influenced chemical physics to a great extent [2]. Although most of the work in this area is theoretical a few intriguing experiments have also been performed [3,4]. The basic problem is one of understanding the quantum behaviour of a molecule when its classical dynamics show a transition from regular to chaotic motion. Regular excited states are important in developing a state specific chemistry [5].

An explicit comparison of classical to quantum dynamics would require the solution of the time dependent Schrodinger equation. However, for the conservative hamiltonians the wavefunctions, at any instant of time, can be written as a linear combination of the eigenfunctions. Therefore conclusions can be drawn by studying the behaviour of the time-independent eigenvalues and eigenfunctions of the molecule. Thus it has been found that the nodal structure of the eigenfunctions has a regular pattern at energies where the phase space is occupied by quasiperiodic trajectories and irregular patterns for the chaotic regions of phase space [2]. Hose and Taylor [6] demonstrated that if an eigenstate $|\psi_m\rangle$ has a projection on a basis function $|\varphi_l\rangle$ greater than 0.707 i.e.

$$| < \varphi_l | \psi_m > |^2 > 0.5 \qquad (1)$$

then the quantum numbers which are used to assign φ_l are almost good quantum numbers for ψ_m. Such a state can be characterized as regular. As far as the eigenvalues are concerned it has been shown that the distribution of the spacing of neighboring levels is Poisson-like for regular states [7] and Wigner-like [8] for chaotic states.

The above criteria, and a few others proposed in the literature [2] are not exact definitions of quantum chaos since there are limitations in their application. However, after the plethora of studies on model [9] and realistic potentials [10], a general conclusion can be drawn: when the regular/irregular regions of phase space are large enough compared to $\hbar$, then the corresponding eigenstates also show regular/irregular behaviour. It turns out that generally there is a "slaggishness" in the transition to molecular quantum chaos. Nevertheless it is not an overstatement to say that the phase space structure, particularly at high excitation energies where quantum calculations are difficult, is a good diagnostic for tracing regular localized or resonant states. These regular regions, which are usually embedded in the chaotic sea, may have a significant effect in dynamical processes. An example is a recent study on the isomerization process of HCN → HNC [11]. It has been shown that a multiple resonance among the vibrational modes, located at the top of the barrier to isomerization, inhibits the reaction.

Van der Waals (vdW) complexes seem most appropriate to further investigate the regular/chaotic correspondence between classical and quantum molecular mechanics. This is because of the relatively small number of bound states, which vdW species can support, and therefore small density of states which implies that the differences between classical and quantum mechanics will be more pronounced. A recent study on the rotationless HCl-Ar [12] has shown that classical chaos appears at very low energies, lower than the zero point energy. In quantum mechanics chaos is reflected in the complexity of the nodal patterns found in the eigenfunctions of the complex.

In this article we report results on the CO-Ar complex. We study the role of rotational excitation in the quantum chaotic behaviour of the system. There are, compared to vibrational studies, only a few investigations of irregular behaviour induced by rotational excitation [13].

Experimentally the breakdown of regular rotational structure through Coriolis interactions is a promising area of study. For example stimulation emission pumping experiments on formaldehyde have demonstrated the importance of Coriolis coupling in mixing vibrational states [4]. CO-Ar is also amenable to experimental observations [14].

2. Computational methods

A pairwise additive interaction potential was used [15]. This consists of two 6-exp Buckingham functions which describe the C-Ar and O-Ar interactions and an extended Rydberg type function for the diatomic CO [16]. The potential has a triangular minimum below the Ar-CO dissociation limit of 105 cm^{-1}. The potential barriers to the linear configurations Ar-O-C and Ar-C-O are 30 cm^{-1} and 50 cm^{-1} respectively. The potential is steeper for Ar approaching C than O which, as we shall see, has an influence on the first excited bending states.

The classical trajectories were integrated in a six dimensional configuration space described by $\underline{r}$, the distance of O from C, and $\underline{R}$, the distance of Ar from the center of mass of CO. The details are given in ref. [17]. The aim of this study was to investigate the effect of the chaotic motion of Ar on the CO oscillator and the flow of rotational energy initially put on CO to the other degrees of freedom. The characterization of the trajectories as regular/chaotic was made by studying the autocorrelation function of the diatomic frequency fluctuations;

$$C_\omega(\tau) = \lim_{T\to\infty} \frac{1}{T} \int_0^T \Delta\omega(t+\tau)\, \Delta\omega(t)\, dt \Big/ \int_0^T \Delta\omega^2(t) dt \qquad (2)$$

Regular motion of Ar relative to CO results in an oscillatory autocorrelation function whereas chaotic motion gives a decaying, usually multiexponential, curve.

The quantum calculations involve the solution of the time independent Schrodinger equation in a body fixed coordinate system (R,r,θ). Where $\cos\theta = \underline{r}.\underline{R}/|\underline{r}.\underline{R}|$. The z-axis was embedded along the R coordinate [19]. In a given body fixed system the vibrational and rotational coordinates can be identified along with the Coriolis coupling terms. The ro-vibrational hamiltonian is generally written [20];

$$H = K_V + K_{VR} + V(r,R,\theta) \tag{3}$$

K_V is the vibrational hamiltonian

$$K_V = -\frac{\hbar^2}{2\mu R}\frac{\partial^2}{\partial R^2}R - \frac{\hbar^2}{2\mu_d r}\frac{\partial^2}{\partial r^2}r - \frac{\hbar^2}{2}\left(\frac{1}{\mu R^2}+\frac{1}{\mu_d r^2}\right)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) \tag{4}$$

where μ and μ_d are the CO-Ar and CO reduced masses respectively. K_{VR} describes the rotation of the system together with the coupling of rotation to vibration. It is a null operator for J=0 states. Its explicit form is given in ref. [20].

The calculations, which are variational in nature, used the angular basis functions which are products of spherical harmonics and the rotation matrix;

$$\Phi^{J,M}_{j,k} = Y_{j,k}(\theta,\gamma)\, D^{J*}_{M,k}(\alpha,\beta,0) \tag{5}$$

where α, β and γ are the three Euler angles for the rotation of the body fixed to space fixed system. These basis functions ensure the correct quantum number of the total angular momentem J, and its projection M, on the z-spaced fixed axis. k is the projection of the total angular momentum on the body fixed z-axis and j the CO angular momentum. These functions are symmetrised to the total parity of the system [20].

Assuming a polynomial Legendre expansion for the potential

$$V(r,R,\theta) = \sum_{\lambda} V_\lambda(r,R)\, P_\lambda(\cos\theta) \tag{6}$$

it can be shown that coupling of different j states occurs only through the potential function;

$$< j,k \mid V \mid j',k' > = \delta_{kk'} \sum_{\lambda} g_\lambda(j,j',\lambda)\, V_\lambda(r,R) \tag{7}$$

where g_λ are the Gaunt coefficients [19]. On the other hand coupling between different states is obtained only through the kinetic operator K_{VR}.

$$<\Phi^{J,M}_{j,k} \mid K_{VR} \mid \Phi^{J,M}_{j',k'}> = \left[\frac{J(J+1)-2k^2}{2\mu R^2}\right]\delta_{kk'}\delta_{jj'} - \delta_{jj'}\frac{\hbar^2}{2\mu R^2}\left[C^{+}_{J,k}\, C^{+}_{j,k}\, \delta_{k'(k+1)} + C^{-}_{J,k}\, C^{-}_{j,k}\, \delta_{k'(k-1)}\right] \tag{8}$$

where

$$C^{\pm}_{jk} = [\, j(j+1) - k\,(k\pm1)]^{1/2} \tag{9}$$

The maximum coupling is for k=0. For van der Waals systems this coupling is ofte neglected meaning that k is a good quantum number.

To identify the regular character of the eigenstates we examine the magnitude of tl expansion coefficients according to Hose-Taylor criterion and we inspect the nodal structu of the projections of wavefunctions on (R,θ) plane. In these calculations r is frozen to i equilibrium value. Nevertheless we have another three variables of the wavefunction t define. These are the three Euler angles which are taken equal to zero. In this case tl body fixed and space fixed axes coincide. Plots of the (R,θ) coordinate with α=β=γ=0 hav the effect of projecting out the M=k=0 components of the wavefunctions.

3. Results and Discussion

The classical dynamics of the rotationless CO-Ar shows an early transition to chaoti behaviour as was found for HCl-Ar [12]. Chaos is associated with the R-stretching an θ-bending modes whereas the diatomic vibrational action variable is adiabatically conserved The chaotic motion of Ar results in a randomization of the phase of CO oscillator as can b deduced from the decaying autocorrelation function of frequency fluctuations in fig.1. Only fo energies as low as 0.001 eV above the minimum of the CO-Ar interaction potential, doe C_ω shows an oscillatory behaviour. Further excitation of the R-stretching mode results in strong mixing with the bending mode [17].

On rotationally exciting the CO the opposite trends are observed. For low j excitation there is strong mixing of j with the bending mode and finally with the R-stretching mode a well. At appropriate energies rotational predissociation can be seen. For higher j values (j>10) large variations of j occur only during a hard collision of Ar with CO. As j increases further it gradually becomes an adiabatic invariant. At this situation we have decoupling of the R-coordinate from the bending mode and the motion of the system becomes regular. The dynamics is mainly governed by the repulsive part of the potential and the changes of j can be described by a kicked rotor model [17].

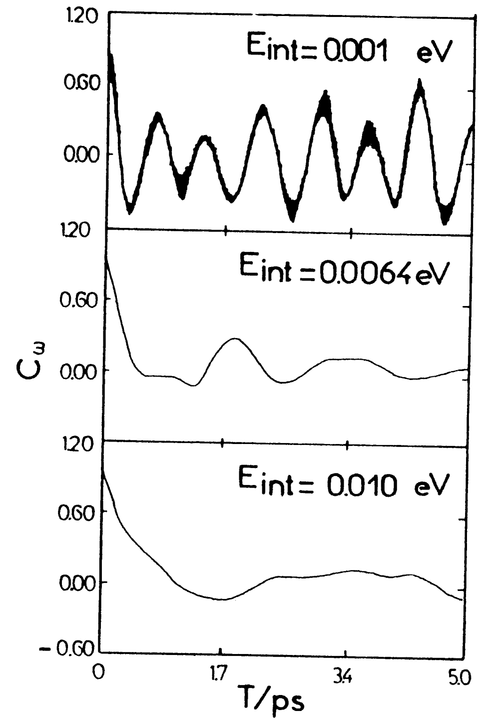

Figure 1

The vibrational CO frequency autocorrelation function at different interaction energies and for initial j=v=0.

Fig.2 shows the time variation of j along with other dynamical variables for a trajectory at 0.001 eV and initially j=10. It can be seen that significant variations of j happen each time R reaches its smallest turning point. That the trajectory behaves regularly can be deduced from the regular oscillations of C_ω.

How does the system behaves quantum mechanically? For J=0 we obtained 21 bound states. These states were computed by performing variational calculations using a basis set comprising all Legendre polynomials with j<10 for the θ coordinate and all Morse oscillator-like functions (R_e=8a_0, D_e=0.005 E_h, ω_e=6x10^{-5} E_h [19]) with n<16 [18]. This basis is sufficient to converge the lower states to very high accuracy. Although with a variational calculation we cannot dismiss the possibility of there being further bound states, these are likely to be very diffuse and weakly bound if they exist at all.

Apart from the ground state the only states which show regularity in their nodal patterns and localization in the configuration space are those shown in figures 3a, 3b and 3c. They have no R-stretching excitation and can be assigned 1,2 and 3 quanta in the bending mode respectively. States with stretching excitation, apart from the first one, show relatively complex nodal patterns and they tend to occupy the whole available configuration space (fig.4).

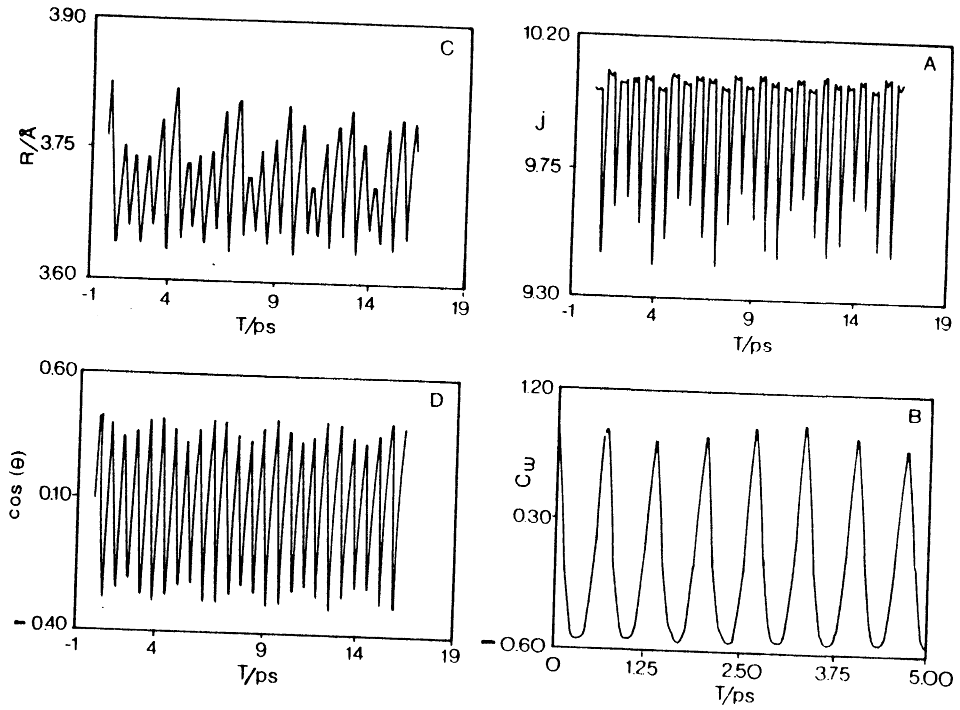

Figure 2

The time variation of some dynamical variables for a trajectory at the interaction energy of 0.001 eV and initially v=0 and j=10.

J>0 calculations were performed using a two-step variational procedure [20]. The 80 lowest solutions of each problem for which k was assumed to be a good quantum number, were used to solve the full problem. This number of functions is much larger than is required for convergence, but was chosen to insure that we obtained most of the bound states of the system.

Results were obtained with k treated as a good quantum number (no Coriolis coupling) together with the fully coupled calculations. Results for the first twenty even parity states for J=10 are given in table 1. Figures 3d, 3e and 3f are the results of calculations with no Coriolis coupling and 3g, 3h and 3i results from fully coupled calculations projected along α=β=γ=0. As can be seen these two sets of figures show only minor changes compared to those of J=0.

Table 1

Lowest 20 levels of the Ar-CO van der Waals complex with J=10 . Frequencies are relative to dissociation of the complex. **k** is the quantum number of the projection of the total angular momentum on the body fixed z-axis. **i** describes the ordering of the levels within a given **k** manifold, which is obtained during the first variational step with **k** treated as a good quantum number.

Level	Frequencies /cm^{-1}		Assignment					
	No Coriolis	Full	k	i	coeff.	k	i	coeff.
1	-77.0	-77.1	0	1	0.99			
2	-74.3	-74.5	1	1	0.98			
3	-67.3	-67.5	2	1	0.98			
4	-63.4	-63.4	0	2	0.98			
5	-56.6	-57.0	1	2	0.90			
6	-56.3	-56.6	3	1	0.97			
7	-54.0	-53.8	0	3	0.95			
8	-50.5	-51.0	1	3	0.96			
9	-46.8	-46.8	0	4	0.95			
10	-46.2	-46.3	2	2	0.94			
11	-44.1	-43.9	0	5	0.96			
12	-42.9	-43.3	2	3	0.96			
13	-41.5	-41.8	4	0	0.98			
14	-38.1	-39.3	0	6	0.77	1	4	0.54
15	-37.8	-37.0	1	4	0.65	1	5	0.56
16	-36.2	-35.7	0	6	-0.51	1	5	0.73
17	-32.1	-32.7	1	6	-0.59	3	2	0.67
18	-31.6	-32.3	1	6	0.67	3	2	0.64
19	-31.5	-31.8	3	3	0.96			
20	-30.3	-29.8	0	7	0.95			

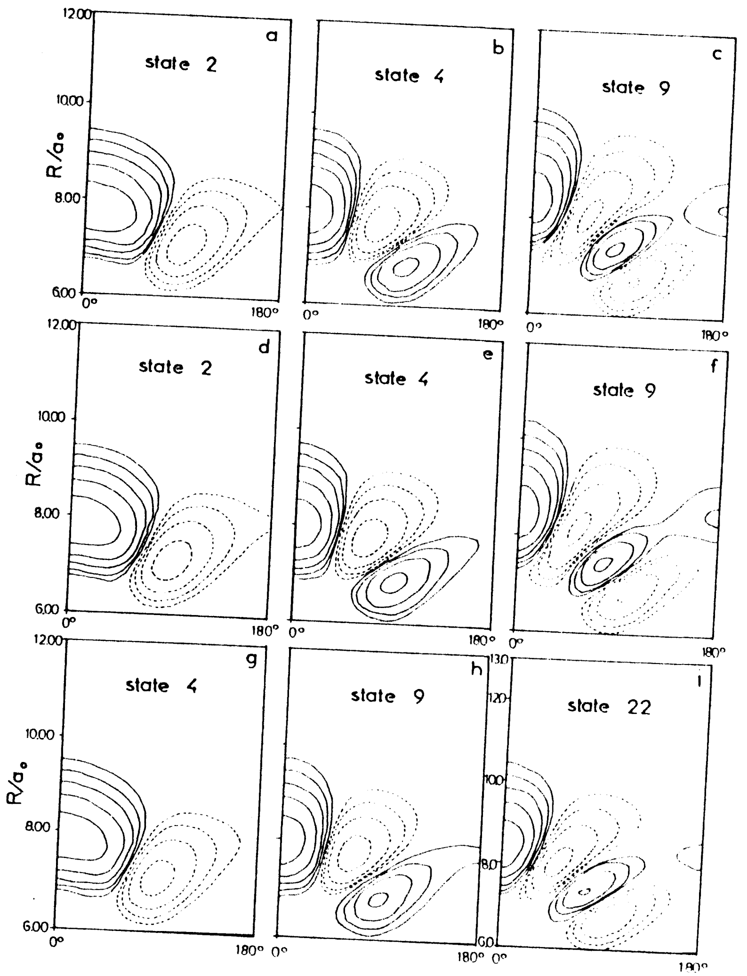

Figure 3

Nodal structure for bending excited states. Contours link points where the wavefunction has 4%, 8%, 16%, 32% and 64% of the maximum amplitude. Solid (Dashed) curves are for positive (negative) amplitude. 3a, 3b and 3c are for J=0 states. 3d, 3e and 3f are for J=10 but k=0 treated as a good quantum number. 3g, 3h and 3i are for fully coupled J=10 states (see text).

The fact that the projections of the eigenfunctions on the (R,θ) plane are independent of the rotational motion, is considered an indication of the conservation of **k**. Similar results were obtained in the 3-d vibrational calculation of HCl-Ar [12]. In that case, the projections of the wavefunctions on the (R,θ) plane did not change when the vibration of HCl was included in the calculations.

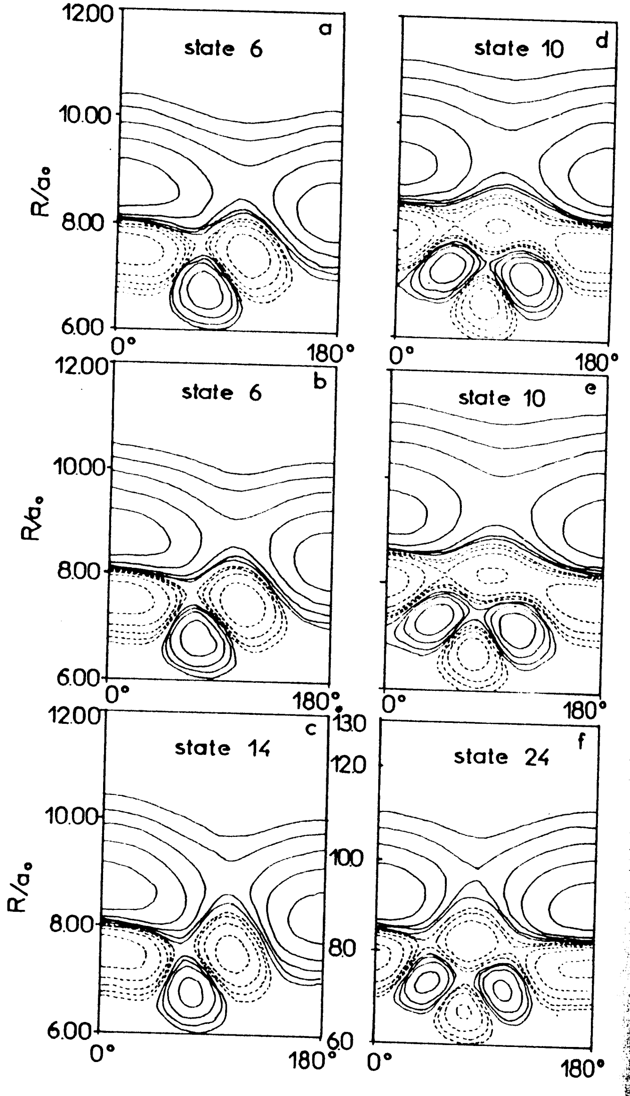

Figure 4

As figure 3 but for states with stretching excitation a) J=0, b) J=10, k=0, and c) J=10, fully coupled calculations.

Inspection of the coefficients in the basis set expansion of the second variational step indeed show that most of the eigenfunctions are characterized by a predominant coefficient (with a particular value of k) which satisfies Hose-Taylor criterion (see table 1). However the highest levels in the fully coupled calculations show differences compared to the highest states of J=0 and J=10 with the Coriolis coupling turned off. Figure 5 shows states close to the dissociation limit. The state from the fully coupled calculations (fig.5c) show smaller complexity in its nodal structure.

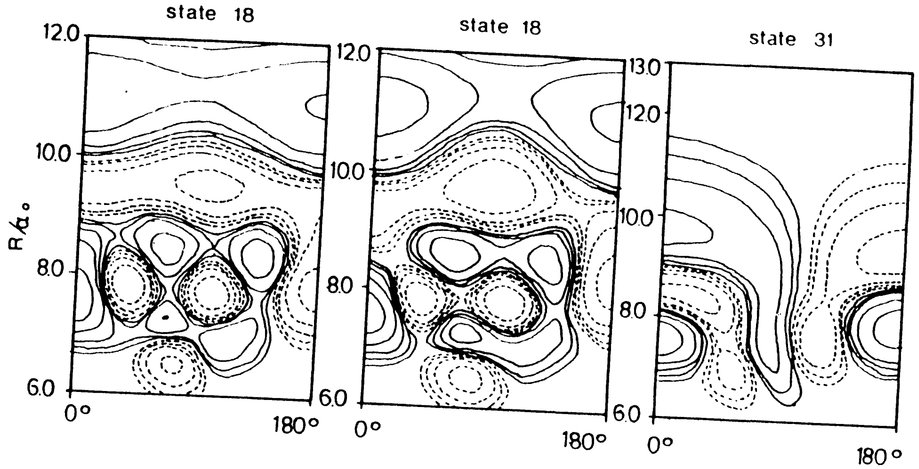

Figure 5

As figure 3 but for states close to the dissociation limit. a) J=0, b) J=10, k=0 and c) J=10 fully coupled states.

From the above results the following conclusions can be drawn:

1. The vibrational states with one, two, and three quanta in the bending mode but none in the stretching are regular and localized. R-stretching excitations produce irregular eigenstates. These trends are in qualitative agreement with the classical dynamics. Regularity in the trajectories is observed only at low interaction energies and by increasing the rotation of CO (fig.2).

2. k is an almost good quantum number for CO-Ar. Since coupling among zero order states of different k occurs through the Coriolis term (Eq.(8)), it is concluded that this part of the hamiltonian does not contribute to the mixing of the basis functions.

3. The irregular character of wavefunctions should be attributed to the potential coupling of states with different j (Eq.(7)). The classical dynamics has shown that by increasing j the system becomes more regular. This is reflected in the highest quantum states of CO-Ar for which terms with large j values in equation (7) make a significant contribution.

4. In the classical calculations it was shown that the fluctuation in j are mainly due to the hard collisions of Ar to CO. Therefore, we consider the repulsive part of the potential as the case for erratic behaviour of the wavefunctions. It is the portion of the potential which has the greatest anisotropy in a Legendre expansion, Eq.(7), and hence causes the greatest mixing between j's.

References

1. A.J. Lichtenberg and M.A. Lieberman, "Regular and Stochastic Motion", (*Springer-Verlag*, N.Y. 1983)

2. D.W. Noid, M.L. Koszykowski and R.A. Marcus, *Ann. Rev. Phys. Chem.*, 32, 267, 1981; E.B. Stechel and E.J. Heller, *Ann. Rev. Phys.* Chem., 35, 563, 1984

3. R.L. Sundberg, E. Abramson, J.L. Kinsey and R.W. Field, *J. Chem. Phys.*, 83, 466, 1985

4. H.L. Dai, C.L. Korpa, J.L. Kinsey and R.W. Field, *J. Chem. Phys.*, 82, 1608, 1985

5. N. Bloemberger and A.H. Zewail, *J. Phys. Chem.*, 88, 5459, 1984

6. G. Hose and H.S. Taylor, *J. Chem. Phys.* 76, 5356, 1982

7. M.V. Berry and M. Tabor, *Proc. Royl. Soc.* London, A356, 375, 1977

8. O. Bohigas, M.J. Giannoni and C. Schmidt, *Phys. Rev. Lett.* 52, 1, 1984

9. E.J. Heller and R.L. Sundberg in "Chaotic Behaviour in Quantum Systems", edited by G. Casati (*Plenum Publishing Co*, 1985)

10. S.C. Farantos and J. Tennyson in "Stochasticity and Intramolecular Redistribution of Energy", edited by R. Lefevbre and S. Muckamel (*Reidel Pub. Co.*, Orsay, 1987)

11. M. Founargiotakis, S.C. Farantos and J. Tennyson, *J. Chem. Phys.*, submitted

12. J. Tennyson, Mol. Phys., 55, 463 (1985); S.C. Farantos and J. Tennyson, *J. Chem. Phys.*, 85, 641, 1986

13. T. Uzer, C.A. Natanson and J.T. Hynes, *Chem. Phys. Lett.*, 122, 12, 1985

14. D.J. Diestler, *J. Chem. Phys.*, 60, 2692, 1974

15. K. Mirsky, *Chem. Phys.*, 40, 445, 1980; J. Manz and K. Mirsky, *Chem. Phys.* 40, 457, 1980

16. J.N. Murrell, S. Carter, S.C. Farantos, A.J. Varandas and P. Huxley, "The Molecular Potential Energy Function", *J. Wiley*, 1984)

17. S.C. Farantos and N. Flytzanis, *J. Chem. Phys.*, in press

18. J. Tennyson, J. Miller and B.T. Sutcliff, *Faraday Discussions*, in press

19. J. Tennyson, *Computer Phys. Comms.*, 42, 157, 1986; *Computer Phys. Report*, 4, 1, 1986

20. J. Tennyson and B.T. Sutcliffe, *Mol. Phys.*, 58, 1067, 1986