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Beyond Ro-vibrational Separation

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Results are presented for nuclear motion calculations on D_3^+, H_2D^+ and the van der Waals complex ArCO in rotationally excited states. These calculations are performed using a two-step variational procedure which allows large ro-vibrational interactions (Coriolis couplings) to be treated accurately. The difficulty of assigning states in systems such as H_2D^+ where the Coriolis interactions are large is illustrated and the limitations of effective Hamiltonians derived from perturbation theory discussed.

Conventional wisdom, as built up over many years by spectroscopists, is that the nuclear motion of most molecules can be well understood in terms of small-amplitude vibrations and near-rigid rotations of the nuclei about some fixed point on the potential-energy surface. Theoretically these ideas are underpinned by the ro-vibrational Hamiltonian due to Eckart[1] and Watson,[2] and by the perturbative analysis of molecular spectra.

Although rotations and vibrations are often treated separately, it is well known that their interaction, through so-called Coriolis forces, can be significant. However, for most spectroscopic purposes, it is normally considered sufficient to consider Coriolis interactions in isolated cases, usually involving accidental or near degeneracy.

In the increasingly lively area of molecular vibrations, to which this meeting is a testimony, theoreticians have, until very recently, been content to study problems in which ro-vibrational interactions were small or even completely neglected.[3,4] This state of affairs was encouraged by the difficulty in performing calculations on polyatomic molecules with anything but the lowest levels of total angular momentum, J.

Recently, a two-step variational procedure was proposed[5] as a way round this computational bottleneck. This and a similar method[6] have now been implemented with a variety of vibrational procedures.[5-9] Fully coupled calculations on molecules with $J > 5$ are now available for H_2D^+,[5] H_3^+,[10] CH_2^+,[11] ArCO[12] and H_2O.[6,9]

Experimental studies have also been performed on spectral regions where the usual perturbative Hamiltonians may no longer be valid.[13] Recent studies on formaldehyde[14] and acetylene[15] have probed regions where ro-vibrational couplings appear to have destroyed completely the structure of the spectrum.

In this paper we discuss the problems that arise when one begins to explore the region where rotational and vibrational motion is inextricably coupled. We will do this with the aid of theoretical calculations on the H_2D^+ and ArCO molecules. These provide a suitable contrast as the large rotational constants of H_3^+ and, especially, its asymmetric top isotopomers lead to strong ro-vibrational coupling, whereas Ar—CO is typical of the van der Waals complexes for which the Coriolis interactions have often been ignored.[3,4]

Method

The methods used to study ro-vibrational coupling effects have to be capable of treating relatively high values of the total angular momentum quantum number, J. Because of the linear increase in size of the secular problem with J, conventional one-step variational procedures have never been applied to problems with $J > 4$. The basic idea behind the two-step procedures that have been used is that the Hamiltonian of the problem can be partitioned thus

$$\hat{H} = \hat{K}_V + \hat{K}_{VR} + V(\boldsymbol{Q}) \tag{1}$$

where the kinetic energy operator has been divided between a vibration-only operator and a vibration-rotation operator which is null for $J = 0$. The potential, V, depends purely on the internal coordinates, $\boldsymbol{Q}$, of the system.

Although there is no unique form for the Hamiltonian of the nuclear motion problem, any body-fixed Hamiltonian can be represented in this way. The idea behind the two-step variational approach is that if $\hat{K}_{VR}$ is only treated approximately then it is possible to decouple the resulting vibrational problem. The solutions of the decoupled problems are then used as a basis set to expand the full problem. Clearly if all functions from the first step are retained in the second then the basis has merely been transformed. However, the savings come because in the second step not all functions are usually required to obtain satisfactory convergence and the resulting secular matrix has a simplified structure.

Exactly how this procedure is implemented depends on the nature of the Hamiltonian, *i.e.* on the choice of internal coordinates and the embedding of the axes. Chen *et al.* (CMW)[6] used solutions of the $J = 0$ problem as expansion functions for their full problem. Tennyson and Sutcliffe (TS)[5] used solutions of problems for which only the off-diagonal Coriolis interactions were neglected. In this case k, the projection of J along the body-fixed z-axis, is a good quantum number. TS employed a Hamiltonian for which there is a range of different methods of defining the body-fixed z-axis.[16] This flexibility is useful as the better the approximation that k is a good quantum number, the fewer the number of functions that will be required for the second step of the calculation.

The method of CMW has the advantage that only one secular problem for the first step need be solved for all J of interest. The TS method requires the solution of $J + 1$ such problems for each J; however, it incorporates the centrifugal distortion term into the first step, producing a basis better adapted to the full problem. As calculations in the very high J regime where centrifugal distortion effects are large are yet to be performed with the CMW method, it is not possible to say definitely which method is the best for studying the ro-vibrational coupling. We note that Carter and Handy[9] have recently followed TS in that they included the diagonal part of the centrifugal distortion term in their first-step Hamiltonian.

A recent refinement of the TS method[17] is to select basis functions for the second variational step according to the energy of the solutions of the first. This gives enhanced convergence over the usual procedure of using the same number of functions for each k. This procedure cannot be implemented with the CMW method.

Calculations

In this section we present the results for two-step calculations on two contrasting triatomic systems. First, we analyse rotationally excited states of isotopomers of H_3^+. These molecular ions have been much studied[18] because of their fundamental nature and the richness of their spectra. Secondly, we consider the Ar—CO van der Waals complex, which is typical of systems for which the ro-vibrational coupling between the levels has often been neglected. All the calculations were performed in scattering coordinates[19] using the program suite SELECT, TRIATOM and ROTLEV.[20]

Table 1 compares results of calculations on D_3^+ with previous calculations[18,21] and experiment[22] for levels with $J \leq 4$. As the molecule has D_{3h} symmetry, special quantum

Table 1. Calculated rotational term values for D_3^+ (in cm^{-1})

level		ground state				ν_1	
		exptl	theory			theory	
J K	s	ref. (22)	this work	ref. (18)	ref. (21)	this work	ref. (18)
1 0		43.61	43.60	43.50	43.70	42.81	42.74
1 1		32.32	32.32	32.24	32.38	31.72	31.67
2 0		130.59	130.55	130.26	130.84	128.20	128.00
2 1		119.37	119.34	119.07	119.60	117.18	116.99
2 2		85.62	85.61	85.42	85.80	83.99	83.87
3 0		260.47	260.40	259.81	261.06	255.72	255.31
3 1		249.35	249.29	248.72	249.91	244.79	244.40
3 2		215.91	215.86	215.38	216.39	211.91	211.59
3 3	+1	159.87	159.83	159.47	160.21	156.78	156.54
3 3	−1	159.87	159.83	159.48	160.21	156.78	156.57
4 0		432.56	432.44			424.69	
4 1		421.57	421.46	420.51		413.89	413.23
4 2		388.53	388.44			381.41	
4 3	−1	333.17	333.09	332.34		326.96	326.46
4 3	+1	333.16	333.08	332.33		326.95	326.45
4 4		255.02	254.91			250.03	
			band origin			2301.25	2301

ν_2

level		$F(J, G, U=-1)$			$F(J, G, U=+1)$		
		exptl	theory		exptl	theory	
J G	s	ref. (22)	this work	ref. (18)	ref. (22)	this work	ref. (18)
1 0	+1	49.73	49.70	49.58			
1 0	−1	53.40	53.37	53.29			
1 1					43.91	43.89	43.82
1 2					12.67	12.67	12.69
2 0	+1	133.63	133.56	133.33			
2 0	−1	144.55	144.50	144.29			
2 1		121.33	121.27	121.06	133.42	133.38	133.19
2 2					100.38	100.36	100.24
2 3	+1					45.65	45.62
2 3	−1				45.65	45.67	45.70
3 0	+1	258.90	258.78	258.34			
3 0	−1	280.50	280.42	280.09			
3 1		247.46	247.35	246.95	268.77	268.69	268.38
3 2		212.52	212.43	212.09	233.94	233.88	233.61
3 3	+1				177.04	176.98	176.77
3 3	−1				177.17	177.11	177.01
3 4					99.03	98.96	98.01
4 0	+1	424.86	424.67	424.01			
4 0	−1	460.35	460.23	459.67			
4 1		413.88	413.70		448.50	448.38	
4 2		380.57	380.42	379.83	412.05	412.94	412.47
4 3	+1	323.67	323.53		354.32	354.22	
4 3	−1	323.71	323.58		354.65	354.55	
4 4					274.06	273.93	273.78
4 5						172.55	
			band origin		1834.67	1835.06	1831.07

Table 2. Comparison of *ab initio* energies (in cm^{-1}) with fitted values for H_2D^+ with $J = 11^{ee}$

level	*ab initio*	fitted	Δ	assignment
1	2348.9	2355.0	6.1	$\nu_0 = 1.00$
2	3002.4	3005.8	3.4	$\nu_0 = 1.00$
3	3438.7	3430.7	−8.0	$\nu_0 = 1.00$
4	3682.3	3671.7	−10.6	$\nu_0 = 1.00$
5	4099.7	4097.8	−1.9	$\nu_0 = 1.00$
6	4253.2	4290.4	37.2	$\nu_2 = 0.87$, $\nu_3 = 0.13$
7	4664.3	4669.4	5.1	$\nu_0 = 1.00$
8	4788.4	4776.4	−12.0	$\nu_2 = 0.14$, $\nu_3 = 0.86$
9	5028.3	5059.0	30.7	$\nu_2 = 0.81$, $\nu_3 = 0.19$
10	5311.1	5326.5	14.6	$\nu_1 = 1.00$
11	5375.5	5349.0	−26.5	$\nu_2 = 0.20$, $\nu_3 = 0.80$
12	5589.9	5599.5	9.6	$\nu_2 = 0.72$, $\nu_3 = 0.18$
13	5759.1	5725.8	−33.3	$\nu_2 = 0.38$, $\nu_3 = 0.62$
14	5896.2	5909.9	13.7	$\nu_2 = 0.71$, $\nu_3 = 0.29$
15	5969.7	5976.7	7.0	$\nu_1 = 1.00$
16	6179.9	6135.6	−44.3	$\nu_2 = 0.40$, $\nu_3 = 0.60$
17	6189.2			$(2\nu_2)$

numbers are required to characterise the rotational levels. Those used here (J, K, s for ν_0 and ν_1, and J, G, U, s for ν_2) are due to Watson.[23] The present calculations employed the accurate potential of Meyer *et al.* (MBB)[24] and reproduce the observed levels closely. Further details of these calculations, including fits to an empirically motivated perturbative Hamiltonian due to Watson[23] can be found in ref. (25). These calculations have been extended to consider the low-lying rotational levels of H_3^+ hot bands.[26]

In tables 2 and 3 we present results for the rotationally excited states of H_2D^+ with $J = 11$ and 15, respectively. Again the calculations used the MBB potential. To obtain results converged to *ca.* 0.1 cm^{-1} it was necessary to include an average of 300 solutions of the first variational step for each k in the second step of the calculation. This gave secular problems of dimension 3600 for $J = 11$ and 4800 for $J = 15$. The exact number of functions with a particular k varied between 232 and 340 because the functions were chosen using the energy-ordering criterion.[17] These results form part of a comprehensive study of the highly rotationaly excited states of H_2D^+, full details of which will be published elsewhere.

Only levels corresponding to the totally symmetric (*ee*) representation are presented in tables 2 and 3. The levels are grouped as manifolds corresponding to the number of rotational levels with this symmetry belonging to the ground and first two (ν_2 and ν_3) vibrational states.

The levels designated fitted in tables 2 and 3 were not obtained by fitting the data presented here. Instead they are the levels given using the parameters fitted to the effective Hamiltonian of Foster *et al.*[27] by Miller and Tennyson.[25] These parameters were obtained by least-squares fits to the calculated levels of H_2D^+ with $J \leqslant 4$. Only Coriolis interactions between the ν_2 and ν_3 vibrational states were allowed for in this fit. Hence the assignments, which were made by matching fitted and calculated energy levels, can only be to pure ν_0 or ν_1 states, or to mixed ν_2/ν_3 states.

The method of assignment by matching *ab initio* and fitted energy levels appears to be reliable for the $J = 11$ results. Here the differences, Δ, though quite sizeable, are considerably smaller than the spacings between the levels. This is not true for the $J = 15$ levels, whose assignments must thus be treated with caution.

Table 3. Comparison of *ab initio* energies (in cm^{-1}) with fitted values for H_2D^+ with $J = 15^{ee}$

level	*ab initio*	fitted	Δ	assignment
1	4121.8	4161.7	39.9	$\nu_0 = 1.00$
2	4992.9	5014.5	21.6	$\nu_0 = 1.00$
3	5633.6	5630.3	−3.3	$\nu_0 = 1.00$
4	5888.2	5981.1	98.7	$\nu_0 = 1.00$
5	6063.4	6083.0	19.6	$\nu_2 = 0.89, \nu_3 = 0.11$
6	6332.7	6275.6	−57.1	$\nu_0 = 1.00$
7	6554.3	6508.4	−45.9	$\nu_2 = 0.12, \nu_3 = 0.88$
8	6818.5	68.06.9	−11.6	$\nu_0 = 1.00$
9	6895.7	7023.3	127.6	$\nu_2 = 0.59, \nu_3 = 0.41$
10	7077.6	7139.1	61.5	$\nu_1 = 1.00$
11	7351.9	7245.9	−106.0	$\nu_2 = 0.40, \nu_3 = 0.60$
12	7449.2	7476.9	27.7	$\nu_0 = 1.00$
13	7651.6	7626.2	−25.4	$\nu_2 = 0.21, \nu_3 = 0.79$
14	7717.3	7834.8	117.5	$\nu_2 = 0.54, \nu_3 = 0.46$
15	7878.5	7980.0	101.5	$\nu_2 = 0.41, \nu_3 = 0.59$
16	7970.6	8000.3	29.7	$\nu_1 = 1.00$
17	8133.7	8214.8	81.1	$\nu_2 = 0.46, \nu_3 = 0.54$
18	8143.7			$(2\nu_2)$
19	8205.6	8215.9	10.3	$\nu_0 = 1.00$
20	8292.2	8366.5	74.3	$\nu_2 = 0.59, \nu_3 = 0.41$
21	8519.6			$(\nu_2 + \nu_3)$?
22	8593.6	8620.8	27.2	$\nu_1 = 1.00$
23	8649.2	8706.7	57.5	$\nu_2 = 0.83, \nu_3 = 0.17$

Table 4. Lowest 15 levels of the Ar—CO van der Waals complex with $J = 5^e$ (frequencies are relative to dissociation of the complex, see text for a discussion of the assignments)

	frequencies/cm^{-1}		assignment					
level	no Coriolis	full	*k*	*i*		*k*	*i*	
1	−82.5	−82.6	0	1	1.00			
2	−80.0	−80.0	1	1	1.00			
3	−72.9	−73.0	2	1	1.00			
4	−68.5	−68.5	0	2	0.99			
5	−62.0	−62.0	1	2	0.41	3	1	0.90
6	−61.9	−62.0	1	2	0.89	3	1	−0.42
7	−59.1	−59.0	0	3	0.98			
8	−55.6	−55.7	1	3	0.99			
9	−51.9	−51.9	0	4	0.99			
10	−51.6	−51.6	2	2	0.99			
11	−48.8	−48.8	0	5	0.99			
12	−48.1	−48.2	2	3	0.99			
13	−47.1	−47.2	4	1	1.00			
14	−42.7	−43.4	0	6	0.76	1	4	−0.62
15	−42.6	−42.1	0	6	−0.55	1	4	0.74

Table 5. Lowest 20 levels of the Ar—CO van der Waals complex with $J = 10^e$ (frequencies are relative to dissociation of the complex, see text for a discussion of the assignments)

	frequencies/cm^{-1}		assignment					
level	no Coriolis	full	k	i		k	i	
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	1	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			

Tables 4 and 5 present results for calculations on the Ar—CO van der Waals complex using the potential-energy surface of Mirsky.[28] The calculations, which kept the CO frozen at its equilibrium bondlength, were performed as part of a comparison of the quantum and classical behaviour of this weakly bound system.[12] These calculations show that the highest truly bound rotational state of ArCO is for $J = 35$.

In tables 4 and 5, the levels of the complex are given relative to dissociation into free Ar and CO. The deepest point on the potential, which corresponds to a bent geometry with the Ar nearer the O, is bound by 105 cm^{-1}. The $J = 0$ ground state is bound by 84.6 cm^{-1}. The projection, k, of J along the Ar—CO coordinate is nearly a good quantum number for this system. Thus only very few functions from the first variational step, 10 for each k, are needed to obtain converged energy levels. The results presented here were actually obtained by including the lowest 80 solutions of the first variational step for each k. The extra functions were included to guarantee convergence of the highest states and because, for this system, the size of the second step of the calculation had little influence on the computer time used.

The Ar—CO levels in tables 4 and 5 are assigned according to the dominant basis functions in the second step of the calculation. The ordering of the levels within a given k manifold is given by i. Thus, within a particular k manifold, $i = 1$ corresponds to the lowest state, $i = 2$ the first excited state *etc.* We note that for $J = 0$, $i = 2$ is the first bending excitation with a frequency of 14.3 cm^{-1} and $i = 3$ is the Ar—CO stretching fundamental which has a frequency of 24.2 cm^{-1} for this potential.

For Ar—CO the states are dominated by basis functions with low k. Inspection of the no Coriolis calculations shows that the complex has no bound states with $k \geq 7$.

Discussion

For low levels of the total angular momentum there can be no doubt that the potential of Meyer *et al.*[24] and our ro-vibrational methods combine to give results of high accuracy. This accuracy is unprecedented in the first-principles calculation of vibration–rotation levels of polyatomic systems. For higher rotational levels, where, for example, rotational manifolds of many vibrational states overlap, the situation is less clear. This is due in part to the absence of observed spectra in this region, although we note that Majewski *et al.*[29] have recently extended their H_3^+ data up to $J = 10$. However, there remain considerable difficulties in interpreting, and hence assigning, spectra in the high-J region.

From inspection of the levels in tables 2 and 3, it is clear that these levels are not well reproduced by the parameters obtained by fitting to the low-J levels of the same system. The standard deviation of the original fits were 0.004, 0.01 and 0.008 cm^{-1} for ν_0, ν_2 plus ν_3 and ν_1, respectively. These should be compared with standard deviations of 6.5, 31 and 11 cm^{-1} for the $J = 11$ data and 45, 84 and 42 cm^{-1} for $J = 15$.

These large differences cannot be explained solely in terms of the increased importance of centrifugal distortion. The original fits included all centrifugal distortion terms up to fourth order as well as making some allowance for sixth-order effects. It is clear that Coriolis coupling effects also have a large part to play. $J = 11$ is the lowest value of J for which the rotational manifold of the vibrational ground state begins to overlap that of a vibrational fundamental. By $J = 15$ the ground-state manifold overlaps those of all the fundamentals.

In order to persist with the fitting and interpretation of spectra in this region *via* effective Hamiltonians based on perturbation theory it would be necessary to consider all these overlapping vibrational states simultaneously. While this is technically possible for the fundamentals, it unfortunately does not provide a real solution. The reason for this can be found in the increasing overlap of the rotational manifolds with vibrational excitation. Thus for $J = 15$, the ν_3 rotational manifold would appear to be overlapped from above by the rotational manifolds of ν_1, $2\nu_2$, $\nu_2 + \nu_3$ and $2\nu_3$ in addition to the states below it. These complications can only become worse with further rotational or vibrational excitation. This means that there is no obvious point where the effect of higher vibrational levels can easily be neglected.

In view of these difficulties one is prompted to ask 'why attempt to fit the spectrum at all?' One could abandon the interpretation of the levels and merely stack them on an energy-ordering basis. However, in doing this one loses the power to predict the properties of spectra of the system. In this situation one can no longer estimate which transitions are likely to be intense and therefore promising candidates for observation using propensity rules. Instead one is reduced to having to calculate every transition intensity explicitly. We are currently doing this for the high-J ($J = 10$–30) region of H_2D^+ in the hope that it will reveal insight into the structure of the spectrum.

By contrast to the H_3^+ systems, van der Waals complexes such as ArCO appear well behaved. Our tabulated results for this system show that even for values of the total angular momentum considerably larger than those previously considered, the neglect of off-diagonal Coriolis couplings gives a very good approximation to the exact ro-vibrational energies (although this approximation is known to be poor for transition intensities[30]). However, neglecting these coupling terms can lead to errors when near degeneracies lead to resonance interactions. This is illustrated by levels 14 and 15 for the $J = 5$ calculation.

In ArCO a more complicated situation appears to arise at higher levels of vibrational excitation. There is an increase of interactions between neighbouring states. These interactions often involve several states, see for example levels 14–16 of the $J = 10$

calculation. This behaviour is probably not so much due to large amounts of rotational excitation but has more to do with behaviour of the underlying vibrational states. Even for $J = 0$ the vibrational levels in the near dissociation region of the complex form a complicated manifold. In this region the assignment of quantum numbers, in terms of Ar—CO stretching and bending quanta, is no longer possible. It appears that these levels are sensitive to the perturbation caused by rotational excitation which results in considerable recoupling in the vibrational wavefunction.

Conclusion

In this work we have focussed on two situations where Coriolis interactions cause a significant perturbation of the spectrum. The first is when the rotational manifolds become larger than the vibrational spacings, causing a general overlap of the levels. For small molecules, this is most likely to be important in systems with large rotational constants. The second situation occurs when the underlying vibrations are strongly coupled and are thus sensitive to being perturbed by ro-vibrational couplings. This situation will be found in regions where the potential is significantly anharmonic. It is this that is being observed in the ro-vibrational spectra recently labelled chaotic.[14,15]

There is a third situation which can lead to strong recoupling in the rotational manifold. This occurs when a bent molecule becomes linear. This situation has recently been explored by Carter and Handy,[9] who found for water that even for $J = 7$ there was strong interaction between levels with different k. They also found that to reproduce the observed spectrum of this system it was necessary to adapt the usual force-field representation of the potential-energy surface to enforce the correct behaviour as the molecule becomes linear.

With the exception of the potential due to Schinke *et al.*,[31] all the potential-energy surfaces recently developed for the H_3^+ system concentrate on the region in the immediate vicinity of the equilibrium geometry. These potentials do not behave correctly as the molecule approaches linearity, nor, perhaps more crucially, do they allow the system to dissociate correctly. As there remain many unanswered questions about the dissociation spectra of this system,[32] this is a serious deficiency.

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