Rotational excitation with pointwise vibrational wave functions

Jonathan Tennyson

Citation: **98**, (1993); doi: 10.1063/1.464396

Rotational excitation with pointwise vibrational wave functions

Jonathan Tennyson
Department of Physics and Astronomy, University College London, London WC1E 6BT, UK

(Received 25 January 1993; accepted 4 March 1993)

Finite element methods, particularly the discrete variable representation (DVR), have proved very successful for calculations on highly excited vibrational states. A procedure is given for calculating the corresponding rotationally excited states for triatomic molecules represented by either scattering (Jacobi) or Radau coordinates. By exploiting the quadrature approximation and the transformation between DVR and basis function representations, this procedure greatly simplifies the calculation of the Coriolis coupling matrix elements. The computational expense of the calculation is thus dominated by that of the underlying vibrational problem. Test results are presented for the benchmark molecules H_2S, H_2O and H_3^+.

I. INTRODUCTION

The calculation of high lying vibrational states has taken on a new lease of light with the advent of finite element methods. Particularly popular is the discrete variable representation (DVR) which has applied to a number of triatomic[1–5] and more recently tetratomic[6,7] molecules. Calculations using a DVR in all coordinates have proved particularly powerful for studying large numbers of vibrational states.[8–11]

More recently several groups have extended DVR calculations[2–4,12–15] and other methods[16] to consider the effect of rotational motion on high lying vibrational states. In particular, Light and Choi[12] used an adaptation of Tennyson and Sutcliffe's (TS)[17] two-step method for a 3D DVR for studying rotational excitation of water. Alternatively Tennyson, Henderson and co-workers[2,15,18] have exploited the transformation properties between the DVR and the corresponding finite basis representation (FBR) to perform the second step of the calculation entirely in an FBR and thus in the form originally proposed by TS. This approach has been criticized by Lipkin *et al.*,[13] but has computational advantages which will be discussed below.

In this work a reformulation of the two-step approach is presented, appropriate for triatomic molecules whose wave functions are represented entirely using a DVR. This approach takes advantage of the transformation properties between DVR and FBR to choose the representation in each coordinate which gives the simplest matrix elements. This greatly reduces the cost of constructing the final Hamiltonian for the problem and shifts the emphasis onto finding efficient algorithms for solving the first ("vibrational") step of the calculation. Calculations are presented for the benchmark molecules H_2S ($J = 1$ for the vibrational fundamentals), H_2O ($J = 9$ for the vibrational ground state) and H_3^+ ($J = 1$ for the lowest 150 or so vibrational states).

II. THEORY

The basic idea of TS's two-step approach is, for a given rotational angular momentum J, to first solve a series of problems for which k, the projection of J on the body-fixed z axis is assumed to be a good quantum number. For each J there are $J + 1$ ($k = 0,1,\ldots,J$) such unique ' vibrational' problems. The second step solves the full ro-vibrational Hamiltonian, including the full Coriolis coupling off-diagonal in k, using selected solutions of the first step. The theory for each of these steps, based on representing all vibrational coordinates in a DVR, is presented below.

A. The first step: the 'vibrational' problem

The multidimensional DVR used in this work uses either scattering (Jacobi) or Radau coordinates which can both be represented by the coordinates (r_1,r_2,θ).[19]

Using a finite basis representation (FBR), the Hamiltonian matrix for a triatomic molecule with a given (J, k), where k is assumed to be a good quantum number, can be written[20]

$$\begin{aligned}\langle m,n,j|\hat{H}^{J,k}|m',n',j'\rangle &= \langle m|\hat{h}^{(1)}|m'\rangle\delta_{n,n'}\delta_{j,j'}+\langle n|\hat{h}^{(2)}|n'\rangle\delta_{m,m'}\delta_{j,j'}\\ &\quad+(\langle m|\hat{g}^{(1)}|m'\rangle\delta_{n,n'}+\langle n|\hat{g}^{(2)}|n'\rangle\delta_{m,m'})\\ &\quad\times j(j+1)\delta_{j,j'}+\langle m,n,j|V(r_1,r_2,\theta)|m',n',j'\rangle\\ &\quad+\langle t|\hat{g}^{(i)}|t'\rangle\delta_{j,j'}\delta_{s,s'}(J(J+1)-2k^2), \qquad (1)\end{aligned}$$

where, if the body-fixed z-axis is taken parallel to $\mathbf{r}_1$ then $|t\rangle = |\ m\rangle$, $s = n$ and $i = 1$; conversely if z is along $\mathbf{r}_2$, $|t\rangle = |\ n\rangle$, $s = m$ and $i = 2$.

In this work the angular basis functions $|j\rangle$ are the polynomial portion of associated Legendre functions, $P_{j,k}(\cos\theta)$. The theory does not constrain the form of the radial basis functions provided that they can be expressed as in terms of orthogonal polynomials in an appropriate coordinate. In practice Morse-like and spherical oscillators are often used, both of which are related to associated Laguerre polynomials.[20,21]

In (1), V is the potential, and the radial kinetic energy integrals are given by

$$\langle t|\hat{h}^{(i)}|t'\rangle=\langle t|\frac{-\hbar^2}{2\mu_i r_i^2}\frac{\partial^2}{\partial r_i^2}|t'\rangle, \qquad (2)$$

Phys. **98** (12), 15 June 1993 0021-9606/93/129658-11$06.00

$$\langle t|\hat{g}^{(i)}|t'\rangle=\langle t|\frac{\hbar^2}{2\mu_i r_i^2}|t'\rangle, \tag{3}$$

where $|t\rangle = |m\rangle$ for $i = 1$ and $|t\rangle = |n\rangle$ for $i = 2$. μ_i are the appropriate reduced masses.[19]

A 1D DVR transformation for either of r_1, r_2 or θ is defined in terms of points, η, and weights, w_η, of the N-point Gaussian quadrature associated[22] with the orthogonal polynomials used for the FBR in that coordinate:

$$T_t^\eta=(w_\eta)^{1/2}|t(\eta)\rangle, \tag{4}$$

where $|t\rangle = |m\rangle, |n\rangle, |j\rangle$ for $\eta = \alpha,\beta,\gamma$, respectively. Note that for the angular coordinate, θ, a different grid is generated for each value of $|k|$. The k dependence of the DVR points and transformation will be left implicit below.

The transformation in all coordinates is simply a product of 1D transformations:

$$\underline{T}=T_{m,n,j}^{\alpha,\beta,\gamma}=T_m^\alpha T_n^\beta T_j^\gamma. \tag{5}$$

A three dimensional DVR is obtained by applying the transformation $\underline{T}^T\underline{H}\underline{T}$. The transformed 'vibrational' Hamiltonian, i.e., the one for which k is assumed to be a good quantum number, can be written at the DVR grid points as

$$\begin{aligned}H_{\alpha,\alpha',\beta,\beta',\gamma,\gamma'}^{J,k}=&K_{\alpha,\alpha'}^{(1)}\delta_{\beta,\beta'}\delta_{\gamma,\gamma'}+K_{\beta,\beta'}^{(2)}\delta_{\alpha,\alpha'}\delta_{\gamma,\gamma'}\\&+L_{\alpha,\alpha',\gamma,\gamma'}^{(1)}\delta_{\beta,\beta'}+L_{\beta,\beta',\gamma,\gamma'}^{(2)}\delta_{\alpha,\alpha'}\\&+V(r_{1\alpha},r_{2\beta},\theta_\gamma)\delta_{\alpha,\alpha'}\delta_{\beta,\beta'}\delta_{\gamma,\gamma'},\\&+(J(J+1)-k^2)M_{\alpha,\alpha',\beta,\beta'}^{(i)}\delta_{\gamma,\gamma'},\end{aligned} \tag{6}$$

where $i = 1$ for z embedded parallel to $\mathbf{r}_1$ and $i = 2$ for z along $\mathbf{r}_2$.

In (6), the potential energy operator is diagonal because of the quadrature approximation[23]

$$\begin{aligned}&\sum_{m,n,j}\sum_{m',n',j'}T_{m,n,j}^{\alpha,\beta,\gamma}\langle m,n,j|V(r_1,r_2,\theta)|m',n',j'\rangle T_{m',n',j'}^{\alpha',\beta',\gamma'}\\&\quad\simeq V(r_{1\alpha},r_{2\beta},\theta_\gamma)\delta_{\alpha\alpha'}\delta_{\beta\beta'}\delta_{\gamma\gamma'},\end{aligned} \tag{7}$$

where $(r_{1\alpha},r_{2\beta},\theta_\gamma)$ is the value of (r_1,r_2,θ) at (α,β,γ).

The kinetic energy terms in (6) are obtained by transforming the FBR matrix elements:

$$K_{\eta,\eta'}^{(i)}=\sum_{t,t'}T_t^\eta\langle t|\hat{h}^{(i)}|t'\rangle T_{t'}^{\eta'}, \tag{8}$$

$$L_{\eta,\eta',\gamma,\gamma'}^{(i)}=J_{\gamma\gamma'}\sum_{t,t'}T_t^\eta\langle t|\hat{g}^{(i)}|t'\rangle T_{t'}^{\eta'} \tag{9}$$

$$\simeq\frac{J'_{\gamma\gamma'}\hbar^2}{2\mu_i r_{i\eta}^2}\delta_{\eta\eta'}, \tag{10}$$

again applying the quadrature approximation, and where

$$J_{\gamma\gamma'}=\sum_j T_j^\gamma j(j+1)T_j^{\gamma'}. \tag{11}$$

The extra term, diagonal in k, introduced by rotational excitation is given by

$$M_{\alpha,\alpha'}^{(1)}=\sum_{m,m'}T_m^\alpha\langle m|\hat{g}^{(1)}|m'\rangle T_{m'}^{\alpha'}\simeq\delta_{\alpha\alpha'}\frac{\hbar^2}{2\mu_1 r_{1\alpha}^2} \tag{12}$$

if $i = 1$, when it is diagonal in β, and

$$M_{\beta,\beta'}^{(2)}=\sum_{n,n'}T_n^\beta\langle n|\hat{g}^{(2)}|n'\rangle T_{n'}^{\beta'}\simeq\delta_{\beta\beta'}\frac{\hbar^2}{2\mu_2 r_{2\beta}^2} \tag{13}$$

if $i = 2$, when it is diagonal in α.

Multidimensional DVR calculations are generally set up as a series of coordinate by coordinate diagonalizations and truncations, but this has been extensively discussed elsewhere.[24–26] The final result is a series of eigenenergies for each $\hat{H}^{J,k}$, $\epsilon_h^{J,k}$, and wave function amplitudes at the grid points, $\psi_{\alpha,\beta,\gamma}^{J,k,h}$. As $\hat{H}^{J,k}$ depends only on k^2, solutions are only needed for the $J + 1$ problems with $k = 0,1,\ldots,J$.

B. Second step: ro-vibrational coupling

Unlike vibration basis function, the rotational problem can be fully expanded in terms of a finite set of functions, generally called rotation matrices. These functions can be symmetrized to reflect the rotational parity of the system, given by $(-1)^{J+p}$ with $p = 0,1$; these functions will be denoted $|J,k,p\rangle$ below. To deal satisfactorily with the transition from linear to nonlinear geometries it is usual to couple these rotation matrices with the k dependent angular functions denoted $|j\rangle$ above.[19] The FBR Hamiltonian matrix for the fully coupled vibration–rotation problem can be expressed as

$$\begin{aligned}&\langle m,n,j,J,k,p|\hat{H}|m',n',j',J,k',p\rangle\\&\quad=\delta_{k,k'}\langle m,n,j|\hat{H}^{J,k}|m',n',j'\rangle-(1+\delta_{k,0}+\delta_{k',0})^{-1/2}\\&\qquad\times\delta_{k',k\pm1}\langle t|\hat{g}^{(i)}|t'\rangle\delta_{j,j'}\delta_{s,s'}C_{J,k'}^{\pm}C_{j,k'}^{\pm},\\&\qquad k=p,p+1,\ldots,J,\quad p=0,1\end{aligned} \tag{14}$$

where as before, if the body-fixed z-axis is taken parallel to $\mathbf{r}_1$ then $|t\rangle = |m\rangle$, $s = n$ and $i = 1$; and if z is along $\mathbf{r}_2$, $|t\rangle = |n\rangle$, $s = m$ and $i = 2$. The angular factors are given by

$$C_{\ell,k}^{\pm}=(\ell(\ell+1)-k(k\pm1))^{1/2}. \tag{15}$$

In either an FBR or a DVR, if one uses the solutions of the first step as a basis to expand the full problem, then the first term in (14) is simply $\epsilon_h^{J,k}$. In this case the problem of constructing the Hamiltonian matrix reduces to the one of constructing the second term. In the usual FBR approach this is done by transforming the matrix element $\langle t|\hat{g}^{(i)}|t'\rangle$ to the new basis.[17,20,27] However, in a DVR the number of points used to expand the first step wave function is often fairly large, and these transformations can prove computationally expensive.[2,15] Another difference between FBR and DVR approaches is that in the FBR the angular integral over associated Legendre polynomials is diagonal. This is not so in the DVR.[28] This means using a DVR for the angular coordinate implies an extra transformation. This approach has been applied to a number of

TABLE I. Energies, in cm^{-1}, for H_2S odd $J = 1$ levels relative to the zero of the potential (Ref. 33); comparison of the benchmark calculation of Carter *et al.* (Ref. 33) and results from DVR3D/ROTLEV3 using various coordinate orders in the diagonalization – truncation procedure.

Vibrational band	JK_aK_c	Ref. 33	This work			
			$\theta \rightarrow r_1 \rightarrow r_2$	$\theta \rightarrow r_2 \rightarrow r_1$	$r_1 \rightarrow r_2 \rightarrow \theta$	$r_2 \rightarrow r_1 \rightarrow \theta$
g/s	1 0 1	3311.2	3311.15	3311.15	3311.15	3311.15
ν_2	1 0 1	4501.7	4501.72	4501.72	4501.73	4501.73
$2\nu_2$	1 0 1	5683.5	5683.45	5683.45	5683.46	5683.46
ν_1	1 0 1	5931.3	5931.31	5931.31	5931.34	5931.34
ν_3	1 1 1	5943.3	5943.25	5943.25	5943.31	5943.31
ν_3	1 1 0	5947.5	5947.47	5947.47	5947.53	5947.53

challenging problems,[4,14] and indeed has certain advantages,[28] but recent tests found it to be computationally expensive.[15]

The approach advocated here removes the need, in most cases, for *all* transformation of matrix elements, making the construction of the second step Hamiltonian rapid. As has been discussed above, the quadrature approximation means that the matrix element $\langle t|\hat{g}^{(i)}|t'\rangle$ is diagonal in the DVR [see Eqs. (12) and (13)]. Conversely the angular contribution is diagonal in the FBR. Therefore transforming the wave functions from the first step to an FBR in θ by

$$\psi^{J,k,h}_{\alpha,\beta,j} = \sum_{\gamma} T^{\gamma}_{j} \psi^{J,k,h}_{\alpha,\beta,\gamma} \tag{16}$$

means that no matrix element transformations are required. It should be noted that the above transformation, unlike that of the matrix elements, is one-dimensional and therefore rapid.

In this new DVR^2FBR^1 representation, the Hamiltonian matrix in terms of solutions of the first step is

$$\begin{aligned}\langle h,k,p|\hat{H}|h',k',p\rangle &= \delta_{h,h'}\delta_{k,k'}\epsilon^{J,k}_{h} - (1+\delta_{k,0}+\delta_{k',0})^{-1/2}\delta_{k',k\pm 1} \\ &\times \sum_{\alpha,\beta,j} \psi^{J,k,h}_{\alpha,\beta,j}\psi^{J,k',h'}_{\alpha,\beta,j} C^{\pm}_{J,k'} C^{\pm}_{j,k'} M^{(i)}_{\alpha,\alpha,\beta,\beta} \\ k &= p,p+1,\ldots,J, \quad p=0,1. \end{aligned} \tag{17}$$

The proposed algorithm is thus as follows. For a given J, one solves the $J + 1$ unique Coriolis decoupled 'vibrational' problem, each of which has a final Hamiltonian of dimension N. In principle N can vary with k, but this possibility will not be explored here. The 'vibrational' problems can be solved using program DVR3D.[29] One selects the M lowest energy solutions of these calculations[30] as a basis for the full problem. The angular coordinate of these M solutions are transformed back to an FBR and the Hamiltonian constructed. Because of its sparse nature, only the diagonal elements and $(k,k + 1)$ off-diagonal blocks are computed and stored. The matrix is diagonalised iteratively, a procedure which has proved very successful for programs ROTLEVD[31] and ROTLEV2.[18] As has been previously noted,[32] the $p = 1$ matrix is simply a submatrix of the $p = 0$ problem with the $k = 0$ rows and columns deleted. This matrix thus need not be recalculated. A new program, ROTLEV3, has been developed for this step of the calculation and sample results are presented below.

III. CALCULATIONS

A. H_2S

Initial calculations focussed on reproducing the benchmark calculations of Carter *et al.*[33] on the $J = 1$ levels of H_2S using the potential of Senekowitch *et al.*[34] These calculations were performed in scattering coordinates for all the 4 possible coordinate orderings allowed by program DVR3D[26,29] and for both the r_1 and r_2 embeddings. Table I summarizes the results for a series of calculations with $N = 600$, $M = 150$, the body-fixed z axis embedded along r_1 and an odd parity symmetrized DVR^2 used in the θ coordinate.

All these calculations give results in complete agreement with those of Carter *et al.* However, as would be expected from the analysis of Henderson *et al.*[26] on optimal coordinate ordering in multidimensional DVR calculations, the calculations which considered the θ coordinate first in the diagonalization truncation show faster convergence. Similar results were obtained for calculations using an even symmetry DVR and for the r_2 embedding.

B. H_2O

Henderson *et al.*[15] have recently compared various methods of calculating $J = 9$ levels for the vibrational ground state of water using Jensen's spectroscopically determined potential.[35] This comparison showed that while the different methods gave results of comparable accuracy, the computer time used for essentially similar calculations varied enormously. This is thus a useful problem with which to demonstrate the computational efficiency of the present approach.

Before turning to rotationally excited states of water, it is necessary to consider the vibrational band origins of this molecule. In a recent paper Choi and Light (CL)[10] performed highly accurate 3D DVR calculations on the band origins of water using Jensen's potential. They comment, without explanation, that their results are slightly different from the previous calculations by Fernley, Miller, and Ten-

TABLE II. Calculated ground vibrational state $J = 9$ rotational term values for water in cm^{-1}.

K_a	K_c	Observed[a]	TRIATOM ROTLEVD	DVR1D ROTLEVD	DVR1D ROTLEV2	DVR3D ROTLEV3
0	9	920.169	920.033	920.034	920.035	920.034
1	9	920.211	920.074	920.074	920.073	920.074
1	8	1079.080	1078.979	1078.979	1078.978	1078.979
2	8	1080.386	1080.246	1080.246	1080.245	1080.246
2	7	1201.922	1202.072	1202.072	1202.072	1202.072
3	7	1216.232	1216.063	1216.063	1216.063	1216.063
3	6	1282.919	1283.281	1283.281	1283.280	1283.281
4	6	1340.886	1340.477	1340.477	1340.477	1340.477
4	5	1360.236	1360.178	1360.178	1360.178	1360.178
5	5	1474.981	1474.030	1474.030	1474.030	1474.030
5	4	1477.298	1476.416	1476.416	1476.416	1476.416
6	4	1631.251	1629.539	1629.539	1629.539	1629.539
6	3	1631.384	1629.682	1629.682	1629.682	1629.682
7	3	1810.584	1807.986	1807.986	1807.986	1807.986
7	2	1810.589	1807.991	1807.991	1807.991	1807.991
8	2	2009.805	2006.196	2006.196	2006.196	2006.196
8	1	2009.805	2006.196	2006.196	2006.196	2006.196
9	1	2225.468	2220.725	2220.725	2220.725	2220.725
9	0	2225.468	2220.725	2220.725	2220.725	2220.725
Size of first step, N			800	800	450	800
Size of second step, M			1500	1500	800	1500
CPU time first step / s			73	471	189	446
CPU time second step / s			47	271	16 104	63

[a] J.-M. Flaud, C. Camy-Peyret, and J. P. Maillard, Mol. Phys. **32**, 499 (1976).

nyson (FMT).[36] A close analysis shows that for most of the higher band origins considered CL's results are approximately 0.1 cm^{-1} lower than FMT's. However, for a few levels, all of them assigned to states of high bending excitation by CL, FMT's results are significantly lower.

In fact this comparison is not completely valid. This is because CL found that Jensen's potential behaved unphysically around linear O–H–H geometries, although this only affected levels more than 18 000 cm^{-1} above the ground state. CL actually used a corrected version[37] of Jensen's potential. Furthermore, FMT only claimed band origins converged to 0.1 cm^{-1} (which is after all considerably better than the accuracy of the potential). New $J = 0$ calculations have been performed with CL's amended potential, FMT's basis functions transformed to a DVR grid of 40 angular points and 24 points in each radial coordinate, and a larger final Hamiltonian, $N = 3000$. These yield results in close agreement with CL's.

Table II compares 3D DVR calculations on the $J = 9$ levels of water in its vibrational ground state. All calculations were performed in Radau coordinates. For the formalism presented above, placing the body-fixed z axis parallel to either $\mathbf{r}_1$ or $\mathbf{r}_2$ is equivalent as these coordinates are symmetry related. However, for $J > 0$, choosing a particular embedding breaks the symmetry of the problem. Full symmetrized basis functions can only be defined for calculations which place z parallel to a symmetry axis of the system. Methods of doing this have been proposed by both Sutcliffe and Tennyson[19] and Choi and Light.[10] However, in either case these symmetric embeddings have problems with linear geometries.

A method, utilizing the properties of a DVR, for avoiding these problems was proposed by Tennyson and Sutcliffe[28] and implemented in program ROTLEV2.[18] However, the price of this method is that it is necessary to treat the angular coordinate in the DVR and thus two-dimensional transformations of the angular matrix elements are required. This in contrast to the procedure proposed here, or the usual FBR two-step procedure as implemented in TRIATOM and ROTLEVD.[31] The procedure used by Tennyson and Henderson[2] of transforming the results of DVR1D[18] back to an FBR and then using ROTLEVD also avoids the extra transformations of ROTLEV2.

As all methods give similar results for similar size problems, the most interesting aspect of Table II is computer timings, given in single processor Cray-YMP seconds, for the two steps of the calculation performed by various methods. It should be noted that the FBR calculation given by TRIATOM/ROTLEVD is inevitably favored by using the vibrational ground state to make the comparison as it is not possible to cut DVR calculations below a certain size without loss of accuracy.[38] However, it is not practical to make comparisons for very high lying states, where DVR calculations perform best, as FBR calculations are no longer feasible in this region.

The first step of the DVR calculations is slower than the FBR because, for $N = 800$, the region where final diagonalization of the Hamiltonian dominates has not yet been reached. The 3D DVR calculations were performed on the 23,040 grid points given above. One might therefore expect the construction of the second step Hamiltonian using the DVR vectors, which are the length of the total number of grid points, to take appreciably longer than using the FBR vectors, which are only of length N. Thus, for example, TRIATOM drives ROTLEVD nearly 6 times faster than DVR1D, in both cases one set of matrix elements, in the radial coordinate, needs to be transformed.

DVR1D driving ROTLEV2 is 60 times slower than DVR1D driving ROTLEVD. This is despite the fact that ROTLEV2 allows a fully symmetrized basis to be used and therefore smaller problems are being solved. ROTLEV2 is slow because of the need to transform the matrix elements in both the angular and one of the radial coordinates. In contrast ROTLEV3 is only slightly slower than ROTLEVD driven by TRIATOM. This shows the benefit of making all the transformations diagonal.

C. H_3^+

From the nuclear motion point of view H_3^+ is a challenging and interesting system with much work having been stimulated by the near-dissociation spectra of Carrington and co-workers.[39] The H_3^+ ion is difficult because of its large amplitude motions, the strong Coriolis interactions and the low barrier to linearity at about 12 000 cm^{-1} above the vibrational ground state. In addition the high symmetry of H_3^+ causes problems not only for methods like ours which cannot reflect the full symmetry of the ion,[40] but also for other methods, many of which show different convergence characteristics with different symmetry.

Tennyson and Henderson[2] used earlier versions of DVR1D and ROTLEVD to study the $J = 1$ states of H_3^+ associated with first 41 vibrational bands of the ion. Even at this level they experienced difficulty with convergence. More recently Bačić and Zhang[16] have computed the $J = 1$ levels of H_3^+ for energies up to 18 000–24 000 cm^{-1}, depending on symmetry, above the $J = 0$ ground state of the system.

A detailed study of all the ($J = 0$) vibrational states of H_3^+ has recently been completed using program DVR3D by Henderson *et al.*[11] This work used scattering coordinates, with grid points based on Morse oscillator-like functions for r_1 and spherical oscillators for r_2. An important result of this study was that the quadrature approximation was not valid for the matrix element $M^{(2)}_{\beta,\beta'}$ because of the importance of geometries in the region of $r_2 = 0$. Henderson *et al.* solved this problem by using entire $\underline{M}^{(2)}$ matrix, evaluated (analytically) in the FBR and transformed to the DVR.

All previous studies of rotationally excited states of H_3^+ in scattering coordinates (e.g., Refs. 2, 40, and 42) have used the r_2 embedding. It is the r_2 embedding which requires the elements of $\underline{M}^{(2)}$ matrix and, if this matrix is not diagonal, they must thus be transformed in ROTLEV3. Calculations of this sort were performed as part of this work and found to give reliable results for $J = 1$ states of the low-lying vibrational levels of H_3^+. However even relatively small calculations with this embedding were computationally very expensive and thus they were not pursued.

The alternative approach is to use the r_1 embedding in which case there is no problem with the $\underline{M}^{(1)}$ matrix being diagonal. Fortunately the r_1 embedding is also appropriate for states of H_3^+ which are quasilinear, which are encountered from about 12 000 cm^{-1} above the ground state upwards. Indeed test calculations suggested that Tennyson and Henderson[2] would have avoided many of their convergence problems if they had used the r_1 rather than the r_2 embedding.

A series of H_3^+, $J = 1$, calculations were undertaken closely modelled on the $J = 0$ 3D DVR calculations of Henderson *et al.*[11] These calculations used spherical oscillators with $\alpha = 0$ for both even and odd symmetries and a first step Hamiltonian size, N, of 6500. A series of calculations were performed varying the number of solutions, M, used for the final Hamiltonian. Tables III–VIII present results, by symmetry, for all the $J = 1$ levels of H_3^+ up to 24 000 cm^{-1} above the H_3^+ vibrational ground state. The results of Bačić and Zhang (BZ)[16] are given for comparison.[41] Both works used implementation A[42] of the potential energy surface of Meyer *et al.*[43]

TABLE III. Calculated ground $J = 1, p = 0$ A_1 rotational levels for H_3^+ relative to the $J = 0$ vibrational ground state in cm^{-1}.

	BZ	$M=1800$
1	2627.18	2627.18
2	4998.39	4998.39
3	5653.72	5653.72
4	7107.37	7107.37
5	7875.85	7875.85
6	8582.41	8582.41
7	9169.63	9169.63
8	9749.30	9749.30
9	10 142.50	10 142.50
10	10 658.30	10 658.30
11	10 990.60	10 990.63
12	11 412.88	11 412.87
13	11 713.53	11 713.53
14	12 112.32	12 112.32
15	12375.82	12 375.84
16	12 648.02	12 648.17
17	12 839.08	12 839.10
18	13 342.09	13 342.08
19	13 471.32	13 471.35
20	13 717.44	13 717.48
21	14 129.49	14 129.54
22	14 167.38	14 167.68
23	14 312.34	14 312.56
24	14 548.93	14 548.93
25	14 929.77	14 929.78
26	15 171.28	15 171.47
27	15 268.56	15 268.71
28	15 417.60	15 417.75
29	15 739.40	15 740.21
30	15 921.10	15 921.04
31	16 010.08	16 010.46
32	16 119.17	16 119.25
33	16 520.99	16 521.22
34	16 616.21	16 617.54
35	16 697.30	16 698.06
36	16 766.11	16 765.94
37	16 969.73	16 969.79
38	17 059.63	17 059.89

TABLE III. (*Continued.*)

	BZ	$M=1800$
39	17 335.97	17 335.92
40	17 452.30	17 453.47
41	17 559.68	17 561.01
42	17 688.65	17 689.18
43	17 793.06	17 793.63
44	17 886.54	17 888.51
45	18 066.14	18 066.51
46	18 277.19	18 277.54
47	18 388.73	18 388.82
48	18 479.63	18 480.07
49	18 664.38	18 664.59
50	18 824.79	18 824.78
51	18 998.64	18 999.58
52	19 079.75	19 079.84
53	19 128.16	19 129.00
54	19 245.27	19 246.69
55	19 285.25	19 286.95
56	19 349.66	19 349.96
57	19 435.24	19 435.95
58	19 529.56	19 529.75
59	19 661.11	19 661.30
60	19 898.39	19 899.19
61	19 938.09	19 938.10
62	19 999.24	20 000.73
63	20 069.40	20 069.37
64	20 169.40	20 169.26
65	20 334.12	20 336.20
66	20 543.08	20 543.11
67	20 655.49	20 656.43
68	20 688.41	20 689.60
69	20 759.72	20 760.24
70	20 864.13	20 866.21
71	20 970.79	20 971.83
72	21 096.55	21 097.32
73	21 139.98	21 140.17
74	21 251.10	21 252.23
75	21 367.58	21 369.24
76	21 411.31	21 412.27
77	21 499.92	21 500.99
78	21 622.14	21 623.55

TABLE IV. Calculated ground $J = 1, p = 1$ A_1 rotational levels for H_3^+ relative to the $J = 0$ vibrational ground state in cm^{-1}.

	BZ	This work
1	7581.63	7581.63
2	10 296.91	10 296.91
3	11 626.47	11 626.47
4	12 917.09	12 917.09
5	13 862.37	13 862.37
6	14 663.79	14 663.79
7	15 317.49	15 317.50
8	15 460.40	15 460.40
9	16 095.70	16 095.70
10	16 843.75	16 843.78
11	17 240.36	17 240.35
12	17 832.10	17 832.11
13	17 954.80	17 954.82
14	18 260.74	18 260.74
15	18 585.40	18 585.40
16	19 111.55	19 111.56
17	19 431.67	19 431.58
18	19 782.91	19 782.90
19	20 121.84	20 121.88
20	20 216.32	20 216.24
21	20 601.07	20 601.05
22	20 682.05	20 681.98
23	21 097.59	21 097.71
24	21 413.07	21 413.24
25	21 570.53	21 570.53
26	21 646.26	21 646.20
27	22 093.15	22 093.16
28	22 233.36	22 233.32
29	22 352.80	22 354.77
30	22 615.48	22 615.74
31	22 855.58	22 855.24
32	22 996.38	22 996.57
33	23 277.18	23 278.05
34	23 432.70	23 432.83
35	23 474.80	23 475.04
36	23 752.41	23 752.58
37	23 916.91	23 916.85

TABLE V. Calculated ground $J = 1, p = 0$ A_2 rotational levels for H_3^+ relative to the $J = 0$ vibrational ground state in cm^{-1}.

	BZ	$M = 1800$	$M = 2600$
1	2616.48	2616.49	2616.49
2	4994.29	4994.29	4994.29
3	5644.05	5644.05	5644.05
4	7080.18	7080.18	7080.18
5	7871.15	7871.15	7871.15
6	8573.09	8573.09	8573.09
7	9132.87	9132.87	9132.87
8	9745.95	9745.95	9745.95
9	10 129.92	10 129.92	10 129.92
10	10 652.75	10 652.75	10 652.75
11	10 908.73	10 908.73	10 908.73
12	11 403.25	11 403.25	11 403.25
13	11 686.47	11 686.48	11 686.48
14	12 100.48	12 100.48	12 100.48
15	12 330.24	12 330.25	12 330.25
16	12 496.20	12 496.21	12 496.21
17	12 805.86	12 805.86	12 805.86
18	13 333.99	13 334.09	13 334.09
19	13 429.87	13 429.88	13 429.88
20	13 673.38	13 673.39	13 673.39
21	13 741.64	13 741.66	13 741.66
22	14 127.20	14 127.67	14 127.66
23	14 528.40	14 528.41	14 528.41
24	14 508.28	14 508.34	14 508.34
25	14 907.24	14 907.25	14 907.25
26	14 949.53	14 949.57	14 949.57
27	15 147.93	15 147.90	15 147.90
28	15 302.70	15 302.68	15 302.67
29	15 404.34	15 404.34	15 404.34
30	15 873.15	15 872.90	15 872.90
31	15 913.13	15 912.32	15 912.31
32	16 031.43	16 031.44	16 031.43
33	16 279.79	16 279.80	16 279.79
34	16 532.69	16 532.63	16 532.63
35	16 681.86	16 681.32	16 681.32
36	16 723.36	16 723.06	16 723.06
37	16 818.56	16 818.06	16 818.06
38	16 964.69	16 964.57	16 964.57
39	17 089.31	17 089.30	17 089.30
40	17 310.19	17 310.15	17 310.15
41	17 411.08	17 411.04	17 411.04

TABLE V. (*Continued.*)

	BZ	$M = 1800$	$M = 2600$
42	17 557.34	17 557.31	17 557.31
43	17 682.88	17 682.86	17 682.86
44	17 776.16	17 776.12	17 776.12
45	18 042.54	18 042.52	18 042.52
46	18 173.43	18 173.39	18 173.39
47	18 351.63	18 351.55	18 351.55
48	18 449.43	18 449.41	18 449.41
49	18 481.87	18 481.84	18 481.84
50	18 707.39	18 706.96	18 706.96
51	18 776.30	18 776.21	18 776.20
52	18 854.60	18 854.62	18 854.62
53	18 990.56	18 989.98	18 989.98
54	19 135.09	19 134.98	19 134.98
55	19 228.18	19 227.09	19 227.09
56	19 289.84	19 289.68	19 289.68
57	19 355.32	19 354.89	19 354.89
58	19 511.05	19 510.85	19 510.85
59	19 594.01	19 593.95	19 593.94
60	19 779.35	19 779.12	19 779.12
61	19 818.94	19 818.95	19 818.94
62	19 975.97	19 975.85	19 975.85
63	19 995.06	19 994.90	19 994.89
64	20 132.67	20 132.55	20 132.55
65	20 219.65	20 219.52	20 219.51
66	20 285.37	20 285.26	20 285.26
67	20 517.57	20 516.80	20 516.80
68	20 596.89	20 596.77	20 596.77
69	20 649.19	20 648.58	20 648.58
70	20 713.55	20 713.45	20 713.45
71	20 847.82	20 846.74	20 846.73
72	20 909.01	20 908.65	20 908.65
73	21 032.35	21 030.75	21 030.74
74	21 166.04	21 165.93	21 165.92
75	21 256.33	21 255.73	21 255.72
76	21 305.82	21 305.23	21 305.22
77	21 441.68	21 441.09	21 441.09
78	21 489.20	21 488.90	21 488.89
79	21 586.29	21 586.22	21 586.22

TABLE VI. Calculated ground $J = 1, p = 1$ A_2 rotational levels for H_3^+ relative to the $J = 0$ vibrational ground state in cm^{-1}.

	BZ	This work
1	86.93	86.93
2	3263.19	3263.19
3	4868.95	4868.95
4	6344.89	6344.89
5	7377.98	7377.98
6	7857.76	7857.76
7	9104.49	9104.49
8	9332.72	9332.72
9	10 061.97	10 061.97
10	10 680.57	10 680.57
11	11 059.00	11 059.03
12	11 916.80	11 916.80
13	12 225.66	12 225.65
14	12 612.33	12 612.44
15	12 708.62	12 708.69
16	13 381.25	13 381.25
17	13 572.84	13 572.89
18	14 142.48	14 142.93
19	14 397.72	14 397.96
20	14 766.53	14 766.55
21	15 018.47	15 018.43
22	15 136.72	15 136.84
23	15 289.01	15 288.19
24	15 811.20	15 812.49
25	15 979.88	15 979.92
26	16 106.90	16 107.03
27	16 595.85	16 595.92
28	16 717.62	16 718.50
29	17 226.15	17 226.20
30	17 424.67	17 425.96
31	17 583.16	17 583.44
32	17 657.59	17 658.13
33	17 727.27	17 727.37
34	17 900.51	17 900.95
35	18 317.55	18 318.03
36	18 453.70	18 453.81
37	18 552.91	18 553.09
38	18 788.68	18 788.80
39	19 184.93	19 185.84
40	19 288.04	19 290.00
41	19 482.95	19 483.46
42	19 665.35	19 665.69
43	19 899.19	19 899.57
44	19 975.30	19 977.80
45	20 109.18	20 109.47
46	20 296.90	20 296.63
47	20 594.71	20 595.49
48	20 628.00	20 628.64
49	20 705.08	20 706.45
50	20 942.24	20 943.12
51	21 017.12	21 017.15
52	21 191.40	21 193.37
53	21 358.23	21 359.25
54	21 442.12	21 443.31
55	21 638.00	21 638.97
56	21 711.36	21 712.68
57	21 807.13	21 809.26
58	22 101.59	22 102.14
59	22 200.63	22 202.42
60	22 353.11	22 355.01
61	22 462.33	22 463.09
62	22 573.03	22 573.75
63	22 776.34	22 776.25
64	22 891.00	22 892.42
65	23 060.00	23 062.32
66	23 107.64	23 109.36
67	23 135.39	23 138.17
68	23 385.02	23 387.53
69	23 450.71	23 452.93
70	23 525.73	23 526.64
71	23 641.28	23 644.14
72	23 785.60	23 786.67

TABLE VII. Calculated ground $J = 1, p = 0$ E rotational levels for H_3^+ relative to the $J = 0$ vibrational ground state in cm^{-1}.

		Even		Odd
	BZ	$M = 1800$	$M = 2200$	$M = 1800$
1	64.10	64.10	64.10	64.10
2	2458.04	2458.04	2458.04	2458.04
3	3240.82	3240.82	3240.82	3240.82
4	4841.21	4841.21	4841.21	4841.21
5	5124.47	5124.48	5124.48	5124.48
6	5583.76	5583.76	5583.76	5583.76

TABLE VII. (*Continued.*)

		Even		Odd
	BZ	$M = 1800$	$M = 2200$	$M=1800$
7	6322.91	6322.90	6322.90	6322.90
8	7044.19	7044.20	7044.20	7044.20
9	7322.66	7322.65	7322.65	7322.65
10	7571.06	7571.06	7571.06	7571.06
11	7839.93	7839.92	7839.92	7839.92
12	7987.61	7987.61	7987.61	7987.61
13	8518.86	8518.85	8518.85	8518.85
14	9064.05	9064.04	9064.04	9064.04
15	9206.04	9206.04	9206.04	9206.04
16	9311.05	9310.98	9310.98	9310.98
17	9675.86	9675.86	9675.86	9675.86
18	9989.09	9989.08	9989.08	9989.08
19	10 015.13	10 015.11	10 015.11	10 015.12
20	10 279.74	10 279.74	10 279.74	10 279.74
21	10 658.79	10 658.78	10 658.78	10 658.78
22	10 752.50	10 752.49	10 752.49	10 752.49
23	10 912.18	10 912.18	10 912.18	10 912.18
24	11016.92	11 016.92	11 016.92	11 016.96
25	11 355.20	11 355.16	11 355.16	11 355.16
26	11 588.82	11 588.82	11 588.82	11 588.82
27	11 740.01	11 740.00	11 740.00	11 740.01
28	11 884.28	11 884.27	11 884.27	11 884.27
29	12 143.08	12 143.07	12 143.07	12 143.07
30	12 204.26	12 203.92	12 203.92	12 203.92
31	12 378.96	12 378.96	12 378.96	12 378.96
32	12 495.30	12 495.30	12 495.36	12 495.36
33	12 623.06	12 623.03	12 623.03	12 623.06
34	12 681.89	12 681.84	12 681.84	12 682.04
35	12 721.66	12 721.62	12 721.62	12 721.69
36	12 895.73	12 895.72	12 895.72	12 895.72
37	13 351.21	13 351.05	13 351.05	13 351.05
38	13 410.36	13 410.34	13 410.34	13 410.34
39	13 456.79	13 456.76	13 456.76	13 456.76
40	13 509.98	13 509.97	13 509.97	13 510.01
41	13 652.38	13 652.35	13 652.35	13 652.41
42	13 726.69	13 726.62	13 726.62	13 726.62
43	13 819.89	13 819.88	13 819.88	13 819.90
44	14 087.89	14 087.80	14 087.80	14 087.84
45	14 124.25	14 124.18	14 124.18	14 124.91
46	14 294.52	14 294.47	14 294.47	14 294.49
47	14 330.24	14 330.16	14 330.16	14 330.68
48	14 548.38	14 548.29	14 548.29	14 548.31
49	14 580.02	14 580.00	14 580.00	14 580.01
50	14 777.20	14 777.11	14 777.11	14 777.12
51	14 924.70	14 924.62	14 924.62	14 924.62
52	14 977.82	14 977.78	14 977.78	14 977.79
53	14 996.88	14 995.90	14 995.90	14 995.90
54	15 082.43	15 082.30	15 082.30	15 082.40
55	15 162.92	15 162.75	15 162.75	15 162.88
56	15 208.77	15 208.56	15 208.56	15 208.80
57	15 251.36	15 251.09	15 251.09	15 251.23
58	15 301.92	15 301.83	15 301.83	15 301.95
59	15 430.35	15 430.31	15 430.31	15 430.37
60	15 451.30	15 451.24	15 451.24	15 451.34
61	15 746.22	15 746.06	15 746.06	15 747.80
62	15 887.72	15 887.61	15 887.61	15 888.57
63	15 944.84	15 944.00	15 944.00	15 944.05
64	15 975.33	15 975.14	15 975.14	15 975.21
65	16 019.27	16 019.01	16 019.01	16 019.10
66	16 030.33	16 030.27	16 030.27	16 030.38
67	16 154.99	16 154.82	16 154.82	16 154.99
68	16 274.27	16 273.89	16 273.89	16 273.90
69	16 503.89	16 503.81	16 503.81	16 503.97
70	16 524.70	16 524.41	16 524.41	16 524.47
71	16 613.67	16 613.67	16 613.67	16 614.78

TABLE VII. (*Continued.*)

		Even		Odd
	BZ	$M = 1800$	$M = 2200$	$M=1800$
72	16 693.42	16 693.16	16 693.16	16 694.09
73	16 708.83	16 708.70	16 708.70	16 709.10
74	16 746.76	16 746.36	16 746.36	16 746.55
75	16 803.08	16 802.81	16 802.81	16 802.97
76	16 906.92	16 906.52	16 906.52	16 906.59
77	16 985.09	16 984.86	16 984.86	16 985.17
78	17 088.33	17 087.99	17 087.98	17 088.15
79	17 237.15	17 236.88	17 236.88	17 237.02
80	17 279.59	17 279.34	17 279.33	17 279.42
81	17 382.93	17 382.72	17 382.72	17 383.47
82	17 491.64	17 491.37	17 491.37	17 493.63
83	17 516.78	17 516.18	17 516.18	17 516.33
84	17 538.74	17 538.46	17 538.46	17 539.20
85	17 589.72	17 589.26	17 589.26	17 590.01
86	17 663.02	17 661.84	17 661.83	17 661.97
87	17 728.19	17 726.31	17 726.31	17 726.61
88	17 749.17	17 749.07	17 749.07	17 749.43
89	17 767.92	17 767.49	17 767.49	17 768.66
90	17 841.73	17 841.26	17 841.26	17 841.96
91	17 906.05	17 905.88	17 905.88	17 906.13
92	17 933.16	17 933.01	17 933.01	17 936.05
93	18 035.77	18 035.60	18 035.60	18 035.75
94	18 191.65	18 191.16	18 191.16	18 191.50
95		18 278.20	18 278.20	18 281.11
96		18 315.35	18 315.35	18 316.17
97		18 410.22	18 410.22	18 410.45
98		18 427.48	18 427.48	18 427.55
99		18 441.39	18 441.39	18 442.05
100		18 517.12	18 517.12	18 517.23
101		18 562.91	18 562.91	18 563.02
102		18 650.81	18 650.80	18 651.27
103		18 707.96	18 707.95	18 708.07
104		18 815.22	18 815.22	18 815.59
105		18 886.23	18 886.23	18 887.35
106		19 009.50	19 009.50	19 010.23
107		19 032.15	19 032.15	19 032.67
108		19 102.01	19 102.01	19 103.08
109		19 152.42	19 152.42	19 153.72
110		19 209.73	19 209.73	19 210.45
111		19 232.99	19 232.99	19 235.98
112		19 276.55	19 276.55	19 279.13
113		19 303.86	19 303.85	19 304.52
114		19 347.25	19 347.24	19 348.58
115		19 370.93	19 370.93	19 372.53
116		19 428.89	19 428.89	19 429.24
117		19 469.05	19 469.04	19 469.19
118		19 543.60	19 543.60	19 544.73
119		19 621.26	19 621.26	19 621.67
120		19 726.40	19 726.39	19 727.06
121		19 829.57	19 829.57	19 829.84
122		19 865.77	19 865.76	19 865.99
123		19 928.63	19 928.63	19 930.33
124		19 941.26	19 941.26	19 942.50
125		19 995.97	19 995.97	19 997.91
126		20 025.19	20 025.19	20 025.49
127		20 082.86	20 082.86	20 083.54
128		20 129.43	20 129.43	20 130.80
129		20 133.66	20 133.66	20 133.83
130		20 179.51	20 179.50	20 179.83
131		20 257.96	20 257.96	20 258.01
132		20 278.47	20 278.46	20 280.33
133		20 300.33	20 300.33	20 302.31
134		20 429.54	20 429.54	20 429.85
135		20 488.39	20 488.39	20 489.27

TABLE VII. (*Continued.*)

BZ	Even $M=1800$	Even $M=2200$	Odd $M=1800$
136	20 544.86	20 544.86	20 545.24
137	20 568.67	20 568.67	20 569.29
138	20 582.33	20 582.32	20 582.54
139	20 647.26	20 647.26	20 647.43
140	20 651.19	20 651.18	20 652.67
141	20 742.89	20 742.89	20 744.24
142	20 799.14	20 799.14	20 800.33
143	20 850.42	20 850.42	20 853.29
144	20 899.25	20 899.24	20 899.61
145	20 932.25	20 932.25	20 933.59
146	20 987.03	20 987.03	20 987.62
147	20 997.12	20 997.11	20 998.11
148	21 098.14	21 098.13	21 098.51
149	21 146.35	21 146.35	21 149.10
150	21 200.18	21 200.17	21 200.65
151	21 226.64	21 226.64	21 228.17
152	21 270.47	21 270.46	21 273.74
153	21 319.45	21 319.45	21 320.57
154	21 348.16	21 348.16	21 349.93
155	21 395.78	21 395.78	21 396.11
156	21 420.29	21 420.28	21 421.25
157	21 458.13	21 458.12	21 459.40
158	21 523.21	21 523.21	21 523.81
159	21 540.07	21 540.06	21 540.39
160	21 558.92	21 558.91	21 561.93
161	21 617.23	21 617.23	21 617.60

TABLE VIII. Calculated ground $J=1, p=1$ E rotational levels for H_3^+ relative to the $J=0$ vibrational ground state in cm^{-1}.

	BZ	Even	Odd
1	2609.38	2609.38	2609.38
2	5086.96	5086.95	5086.95
3	5639.90	5639.90	5639.90
4	7100.32	7100.32	7100.32
5	7957.14	7957.14	7957.14
6	8571.60	8571.60	8571.60
7	9216.44	9216.45	9216.45
8	9746.50	9746.50	9746.50
9	10 088.20	10 088.20	10 088.20
10	10 731.24	10 731.24	10 731.24
11	10 994.66	10 994.66	10 994.71
12	11 405.12	11 405.10	11 405.10
13	11 765.05	11 765.05	11 765.07
14	12176.64	12176.64	12176.64
15	12433.96	12433.96	12434.02
16	12677.42	12677.41	12677.67
17	12803.76	12803.75	12803.82
18	13 405.33	13 405.31	13 405.32
19	13 524.35	13 524.35	13 524.39
20	13 727.21	13 727.21	13 727.28
21	14 131.70	14 131.66	14 131.76
22	14 177.12	14 177.10	14 178.00
23	14 350.57	14 350.56	14 350.92
24	14 595.51	14 595.48	14 595.51
25	14 990.19	14 990.18	14 990.21
26	15 179.18	15 179.15	15 179.59
27	15 323.14	15 323.10	15 323.11
28	15 477.22	15 477.23	15 477.32
29	15 763.56	15 763.55	15 763.58
30	15 970.91	15 970.88	15 970.96
31	16038.70	16 038.70	16 039.33
32	16 176.39	16 176.35	16 176.49
33	16 582.96	16 582.95	16 583.00
34	16 708.80	16 708.75	16 709.81
35	16 754.64	16 754.58	16 755.02
36	16 826.77	16 826.75	16 826.79
37	16 991.78	16 991.66	16 991.75
38	17 095.65	17 095.66	17 095.71
39	17 377.35	17 377.33	17 377.43
40	17 507.64	17 507.62	17 511.07
41	17 632.56	17 632.53	17 632.90
42	17 698.28	17 698.25	17 698.93
43	17 825.84	17 825.79	17 825.94
44	18 115.30	18 115.27	18 115.48
45	18 266.90	18 266.82	18 268.56
46	18 318.69	18 318.69	18 320.96
47	18 421.16	18 421.03	18 421.23
48	18 631.28	18 631.23	18 631.46
49	18 766.62	18 766.65	18 766.73
50	18 939.65	18 939.65	18 939.99
51	19 120.80	19 120.55	19 121.30
52	19 162.18	19 162.02	19 163.27
53	19 257.34	19 257.14	19 257.62
54	19 301.76	19 301.47	19 304.08
55	19 367.64	19 367.37	19 368.67
56	19 473.74	19 473.49	19 473.82
57	19 532.35	19 532.36	19 533.50
58	19 662.78	19 662.71	19 663.52
59	19 856.14	19 856.08	19 856.11
60	19 964.73	19 964.81	19 967.18
61	20 055.88	20 056.20	20 057.34
62	20 124.13	20 123.93	20 124.63
63	20 197.80	20 197.80	20 198.57
64	20 211.49	20 211.17	20 211.30
65	20 636.92	20 636.97	20 637.49
66	20 672.35	20 672.06	20 673.43
67		20 728.62	20 728.73
68		20 761.30	20 763.34
69		20 812.29	20 813.98
70		21 017.37	21 018.56
71		21 224.62	21 228.39
72		21 285.63	21 287.50
73		21 332.81	21 333.29
74		21 372.91	21 373.51
75		21 513.03	21 513.40
76		21 559.96	21 560.74
77		21 649.30	21 652.73
78		21 681.78	21 682.28
79		21 756.82	21 758.65
80		21 784.71	21 786.13
81		21 903.09	21 904.03
82		22 078.08	22 079.62
83		22 120.54	22 121.63
84		22 233.32	22 233.61
85		22 267.03	22 269.90
86		22 366.39	22 368.80
87		22 435.99	22 436.73
88		22 576.55	22 577.93
89		22 692.61	22 694.55
90		22 724.49	22 726.36
91		22 840.05	22 840.70
92		22 931.76	22 932.57
93		23 041.17	23 044.65
94		23 091.27	23 092.17
95		23 121.59	23 126.53
96		23 163.15	23 164.46
97		23 303.91	23 304.18
98		23 352.04	23 352.96

TABLE VIII. (*Continued.*)

	BZ	Even	Odd
99		23 369.21	23 369.99
100		23 514.72	23 519.83
101		23 576.85	23 579.02
102		23 652.92	23 654.86
103		23 693.02	23 694.79
104		23 730.07	23 732.75
105		23 848.98	23 849.75
106		23 868.82	23 868.82

The present results show excellent convergence with respect to M. For all symmetries it was found that the $M = 1800$ calculations were converged to within 0.01 cm^{-1}, see Tables V and VII. This means that any error in the calculations is directly attributable to lack of convergence in the first step of the calculation.

BZ only claim convergence of 1 cm^{-1} for their calculations. Generally the present results and BZ's are in closer agreement—within 0.2 cm^{-1} for most states. Indeed this agreement was such that symmetry assignments were made for all levels presented here by direct comparison with BZ's levels.

However, both calculations show differential convergence with respect to symmetry. In particular the present results obtained from even symmetry first step calculations —which give the (A_1, $p = 1$), (A_2, $p = 0$), (E_o, $p = 0$), and (E_e, $p = 1$) symmetries—are much more reliable than the other symmetries generated by the odd first step calculation. In BZ's case the E states appear less well converged than the A symmetry ones. A full study of the behaviour of the very high lying ro-vibrational states of H_3^+ is currently under way[44] using ROTLEV3.

IV. CONCLUSIONS

A method of calculating rotationally excited states of vibrational states of triatomic molecules which have been represented entirely in a discrete variable representation (DVR). The method is shown to be capable of giving results of accuracy competitive to conventional finite basis representation (FBR) methods, to be computationally more efficient than other DVR based procedures and to be particularly useful for studying highly excited vibrational states. It should be noted that, in the studies presented here, the bulk of the computer time was spent on the first step of the calculation. As the time taken for this step scales only linearly with the degree of rotational excitation, the method should be useful for much higher J states than have been studied here.

Finally, it is should be noted that the ability to switch DVR and FBR representations can be used in other situations. In particular it should be possible to derive an efficient algorithm for evaluating dipole transition matrix elements in a similar fashion to the one used above.

ACKNOWLEDGMENTS

I would like to thank James Henderson for many helpful discussions and for persuading DVR3D to drive ROTLEV3 correctly. This work was supported by SERC Grant No. GR/H41744.

[1] Z. Bačić and J.C. Light, Annu. Rev. Phys. Chem. **40**, 469 (1989).
[2] J. Tennyson and J.R. Henderson, J. Chem. Phys. **91**, 3815 (1989).
[3] S.E. Choi and J.C. Light, J. Chem. Phys. **92**, 2129 (1990).
[4] M. Mladenovic and Z. Bačić, J. Chem. Phys. **93**, 3039 (1990).
[5] W. Hau and T. Carrington, Jr., J. Chem. Phys. **97** 3029 (1992).
[6] J.A. Bentley, R. E. Wyatt, M. Menou, and C. Leforestier, J. Chem. Phys. **97**, 4255 (1992).
[7] A. McNichols and T. Carrington, Jr., Chem. Phys. Lett. **202**, 464 (1993).
[8] R.M. Whitnell and J.C. Light, J. Chem. Phys. **90**, 1774 (1989).
[9] J.R. Henderson and J. Tennyson, Chem. Phys. Lett. **173**, 133 (1990).
[10] S.E. Choi and J.C. Light, J. Chem. Phys. **97**, 7031 (1992).
[11] J.R. Henderson, J. Tennyson, and B.T. Sutcliffe, J. Chem. Phys., (in press).
[12] J.C. Light and S.E. Choi, in *Mode Selective Chemistry*, edited by J. Jortner *et al.* (Kluwer, Dordrecht, 1991), p. 67.
[13] N. Lipkin, N. Moiseyev, and P.R. Certain, Theor. Chim. Acta **82**, 47 (1992).
[14] C. Leforestier, J. Chem. Phys. **94**, 6388 (1991).
[15] J.R. Henderson, J. Tennyson, and B.T. Sutcliffe, Philos. Mag. (in press).
[16] Z. Bačić and J.Z.H. Zhang, J. Chem. Phys. **98**, 3707 (1992).
[17] J. Tennyson and B.T. Sutcliffe, Mol. Phys. **58**, 1067 (1986).
[18] J.R. Henderson and J. Tennyson, Comput. Phys. Commun. (in press).
[19] B.T. Sutcliffe and J. Tennyson, Int. J. Quantum Chem. **39**, 183 (1991).
[20] J. Tennyson, Comput. Phys. Rep. **4**, 1 (1986).
[21] J. Tennyson, S. Miller, and J.R. Henderson, in *Methods in Computational Chemistry*, Vol. 4, edited by S. Wilson (Plenum, New York, 1992), p. 91.
[22] A.H. Stroud and D. Secrest, *Gaussian Quadrature Formulas* (Prentice-Hall, London, 1966).
[23] A.S. Dickinson and P.R. Certain, J. Chem. Phys. **49**, 4204 (1968).
[24] Z. Bačić, R.M. Whitnell, D. Brown, and J.C. Light, Comput. Phys. Commun. **51**, 35 (1988).
[25] J.C. Light, R.M. Whitnell, T.J. Pack, and S.E. Choi, in *Supercomputer Algorithms for Reactivity, Dynamics and Kinetics of Small Molecules*, edited by A. Laganà, NATO ASI series C, Vol. 277 (Kluwer, Dordrecht, 1989), p. 187.
[26] J.R. Henderson, C.R. Le Sueur, S.G. Pavett, and J. Tennyson, Comput. Phys. Commun. **74**, 193 (1993).
[27] J. Tennyson, S. Miller, and B.T. Sutcliffe, in *Supercomputer Algorithms for Reactivity, Dynamics and Kinetics of Small Molecules*, edited by A. Lagana, NATO ASI series C, Vol. 277 (Kluwer, Dordrecht, 1989), p. 261.
[28] J. Tennyson and B.T. Sutcliffe, Int. J. Quantum Chem. **42**, 941 (1992).
[29] J.R. Henderson, C.R. Le Sueur, and J. Tennyson, Comput. Phys. Commun. (in press).
[30] B.T. Sutcliffe, S. Miller, and J. Tennyson, Comput. Phys. Commun. **51**, 73 (1988).
[31] J. Tennyson, S. Miller, and C.R. Le Sueur, Comput. Phys. Commun. (in press).
[32] B.T. Sutcliffe, J. Tennyson, and S. Miller, Theor. Chim. Acta **72**, 265 (1987).
[33] S. Carter, P. Rosmus, N.C. Handy, S. Miller, J. Tennyson, and B.T. Sutcliffe, Comput. Phys. Commun. **55**, 71 (1989).
[34] J. Senekowitsch, S. Carter, A. Zilch, H-J. Werner, N.C. Handy, and P. Rosmus, J. Chem. Phys. **90**, 783 (1989).
[35] P. Jensen, J. Mol. Spectrosc. **133**, 438 (1989).
[36] J.A. Fernley, S. Miller, and J. Tennyson, J. Mol. Spectrosc., **150**, 597 (1991).
[37] Actually the correction to Jensen's potential (Ref. 35) suggested in Ref. 10 is rather unsatisfactory as it is defined in terms of Radau coordinates. Radau coordinates are, of course, mass dependent and therefore the potential suggested is also implicitly mass dependent.
[38] J. Tennyson, J. Chem. Soc. Faraday Trans. **88**, 3271, (1992).

[39] A. Carrington, I.R. McNab, and Y.D. West, J. Chem. Phys. **98**, 1073 (1993), and references therein.

[40] J. Tennyson and B.T. Sutcliffe, Mol. Phys. **51**, 887 (1984).

[41] Note that BZ use $p = 0$ and $p = 1$ to denote even and odd rotational parity, respectively. Here the standard notation of giving the parity by $(-1)^{J+p}$ is preferred.

[42] M.J. Bramley, J.R. Henderson, J. Tennyson, and B.T. Sutcliffe, J. Chem. Phys. (in press).

[43] W. Meyer, P. Botschwina, and P.G. Burton, J. Chem. Phys. **84**, 891 (1986).

[44] J.R. Henderson and J. Tennyson (work in progress).