A Computational Study of the Ro-vibrational Spectra of CH_2D^+ and CHD_2^+

Jesse Simmons,^{1, a)} Xiao-Gang Wang,^{1, b)} and Tucker Carrington Jr.*^{1, c)}

*Department of Chemistry and Department of Physics, Queen's University, Kingston,
Ontario K7L 3N6, Canada*

(Dated: 23 October 2019)

Abstract

In this paper we present ro-vibrational energy levels of CH_2D^+ and CHD_2^+ . They are computed with a large basis and the Lanczos algorithm. CH_2D^+ and CHD_2^+ are believed to play an important role in interstellar space, but so far there are no definitive observations. The predictions of this paper should facilitate detection. For CH_2D^+ , two CH stretch bands have been studied at high resolution. Compared to our calculated energies, the root mean square error is 0.08 cm^{-1} . For CHD_2^+ , one CH stretch band has been studied at high resolution. Compared to our calculated energies, the root mean square error is 0.5 cm^{-1} . Errors are larger, for both isotopologues, for bend states. We attribute these errors to the potential energy surface. Wavefunction and probability distribution plots are used to make assignments. The ν_1 band of CHD_2^+ is significantly perturbed and according to our calculations,

the $3\nu_3$ state is closest and might be the most important perturber.

^{a)}Electronic mail: 11js110@queensu.ca

^{b)}Electronic mail: xgwang.dalian@gmail.com

^{c)}Electronic mail: Tucker.Carrington@queensu.ca

I. INTRODUCTION

It is widely believed that ion-molecule reactions involving the methyl cation play an important role in molecular clouds¹. Unfortunately it is difficult to verify these ideas by detecting CH_3^+ because it has no permanent dipole moment. For this reason, scientists would like to detect two of its deuterated counterparts, CH_2D^+ and CHD_2^+ , in interstellar space. Because the centre of mass and the centre of charge of both CH_2D^+ and CHD_2^+ do not coincide, they have non-zero dipole moments, therefore enabling detection²⁻⁴. In this paper we describe the calculation of ro-vibrational spectra of both these molecules. The energy levels we report ought to facilitate the detection of CH_2D^+ and CHD_2^+ .

Understanding the role of deuterated isotopologues is important in the study of star formation. In interstellar clouds, abundance ratios of deuterated molecules to their non-deuterated counterparts are often much larger than the natural D/H cosmic ratio, sometimes up to a factor of 10^4 . It is thought that CH_2D^+ and CHD_2^+ may play a role in the deuteration of these other molecules⁵⁻⁷. The fractionation is driven by reactions in the gas phase and on the surfaces of dust particles. Due to the putative influence of CH_2D^+ and CHD_2^+ in these reactions they are of special spectroscopic interest. Tentative identifications of CH_2D^+ in space by Wooten & Turner (2008)⁸ and Roueff et al. (2013)⁹ have heightened experimental interest in CH_3^+ isotopologues in recent years. Despite substantial experimental efforts to measure the rotational lines of the two molecules^{4,10-17}, there are no variational calculations of their ro-vibrational spectra. In this paper, we report the results of such calculations. Our results agree well with existing high-resolution laboratory measurements. Many ro-vibrational levels are assigned and all are labelled with the appropriate irreducible representation. In addition, low-lying vibrational levels of both molecules are calculated. We confirm the existence of nearly degenerate states that perturb the ν_1 band of CHD_2^+ and complicate its analysis^{11,16}.

Many years ago, a CH stretch fundamental was observed in both CH_2D^+ and CHD_2^+ ^{10,11}. Later, Amano reported the observation of the first pure rotational lines⁴. Asvany and Schlemmer and their colleagues have more recently used a sophisticated action spectroscopy technique to observe two bands of CH_2D^+ and one band of CHD_2^+ ^{14,16}.

For molecules with four atoms it is now straightforward to compute numerically exact ro-vibrational spectra¹⁸⁻²⁵. When a direct product basis is used, the size of the required basis set is large, but because iterative eigensolvers make it possible to determine eigenvalues without com-

puting and storing a Hamiltonian matrix, the calculation is straightforward. To use an iterative eigensolver, one must evaluate matrix-vector products (MVPs). When a direct product basis is used, this is best done by doing sums sequentially. We make use of the symmetry-adapted Lanczos method with which it is possible to calculate states transforming like all of the irreducible representations from a single set of matrix-vector products. There is a previous variational calculation of vibrational ($J = 0$) energy levels of CH_2D^+ and CHD_2^+ . It uses normal coordinates and an approximate N-mode representation of the PES and the inverse moment of inertia matrix¹³.

II. COMPUTING RO-VIBRATIONAL LEVELS

We use the CH_3^+ potential energy surface (PES) of Yu & Sears (YS)²⁶. It was obtained at the CCSD(T) level of theory using an extrapolation approach and cc-pVTZ and cc-pVQZ basis sets. 227 points near equilibrium were used to fit to a quartic polynomial in symmetry-adapted internal coordinates. In an attempt to improve the PES, YS introduced radial and angular scaling factors.

To solve the Schrödinger equation we must: choose coordinates and a kinetic energy operator, choose a basis, and compute eigenvalues. The coordinates are the polyspherical coordinates^{27–29} associated with three Radau vectors³⁰ $\vec{r}_0, \vec{r}_1$, and $\vec{r}_2$, pointing from the Radau canonical point to the H and D atoms as shown in Figure 1 for CHD_2^+ . The coordinates θ_1 and θ_2 are the angles between $\vec{r}_0$ and $\vec{r}_1$, and $\vec{r}_0$ and $\vec{r}_2$ respectively. ϕ_2 is the dihedral angle between the planes $\vec{r}_0 \times \vec{r}_1$ and $\vec{r}_0 \times \vec{r}_2$. The Euler angles α, β, γ specify the orientation of the molecule with respect to a space-fixed frame. The body-fixed z -axis is along $\vec{r}_0$ and the body-fixed y -axis is along $\vec{r}_0 \times \vec{r}_1$. The KEO in these coordinates is well known^{27–29,31}. The masses we use are 1.007825 u, 2.014102 u, and 12.0 u for the H, D, and C atoms respectively³².

We use a parity-adapted basis. Each function in the basis is a product of a parity-adapted bend-rotation function^{33,34} and a potential-optimized discrete variable representation (PODVR) stretch functions^{35–38}. The parity-adapted bend-rotation functions, $u_{l_1, l_2, m_2, K}^{JMP}$ are linear combinations of spherical-harmonic type functions which are themselves products of an associated Legendre function, $\Theta_{l_1, m_1}(\theta_1)$, a spherical harmonic, $Y_{l_2, m_2}(\theta_2, \phi_2)$ and a Wigner function of the Euler angles (α, β, γ) ³⁹. $m_1 = -m_2$. Using parity-adapted basis functions makes it possible to separately calculate even and odd energy levels. In our calculations, the angular labels l_1, l_2 , and m_2 all have the same maximum value ($l_{\max} = m_{\max}$). PODVR function, $f_{\alpha_i}(r_i)$, for a single stretch coordinate are built from 200 sine functions using a potential cut with all other coordinates set to their equi-

FIG. 1. Coordinates for CHD_2^+ . B is the canonical point for the Radau vectors, offset slightly from the central carbon atom (black) which is not labelled. r_0, r_1 , and r_2 are Radau vectors. ϕ_2 is the dihedral angle, θ_1 and θ_2 are the angles between the r_0 and r_1 and the r_0 and r_2 angles respectively.

librium values. The same number of PODVR functions is used for each r_i . The resulting basis functions are of the form,

$$f_{\alpha_0}(r_0)f_{\alpha_1}(r_1)f_{\alpha_2}(r_2)u_{l_1,l_2,m_2,K}^{JMP}(\theta_1, \theta_2, \phi_2; \alpha, \beta, \gamma) \quad (1)$$

To compute energy levels we use a symmetry-adapted variant^{40–42} of the Cullum and Willoughby⁴³ Lanczos algorithm. For a given parity block, it makes it possible to calculate states that are symmetric or anti-symmetric with respect to the permutation of the $\vec{r}_1$ and $\vec{r}_2$ vectors⁴⁴ from a single set of matrix-vector products. The permutation-inversion group of both CH_2D^+ and CHD_2^+ is G_4 . Each state is labelled by A/B, if it is symmetric/antisymmetric with respect to permutation and by +/- if it is symmetric/antisymmetric with respect to inversion⁴⁵.

Matrix-vector products for each term in the kinetic energy operator (KEO) are done separately. They are all simple. Functions of the stretch coordinates are assumed to be diagonal in the PODVR. Matrix elements of angular factors are computed with standard equations^{33,39}. The potential we use is given in terms of symmetrized bond coordinates and our KEO and basis functions are functions of Radau coordinates. To use the potential we must therefore transform from bond coordinates to Radau coordinates and use quadrature for the matrix elements. Potential MVPs are evaluated by doing sums sequentially^{28,36,46,47}. We use Gauss-Legendre quadrature for θ_1 and θ_2 and $n_\theta = l_{\max} + 1$ points. We use equally spaced points in the range $[0, 2\pi]$ for ϕ_2 and a fast Fourier Transform method with at least $2m_{\max} + 1$ Fourier points. For Fourier transform details see Refs.

[47 and 48]. A ceiling of 30000 cm^{-1} is applied to reduce the spectral range of the Hamiltonian⁴⁹.

III. RESULTS

A. Assignment

Vibrational and ro-vibrational levels of both isotopologues were assigned by comparing the levels we compute with those obtained from models. In the vibrational case, we compare variational levels to those calculated from

$$E_{an harm} = \sum_i \omega_i(n_i + 1/2) + \sum_{i \geq j} \chi_{ij}(n_i + 1/2)(n_j + 1/2) , \quad (2)$$

which can be derived using second order perturbation theory⁵⁰.

There are 6 ω_i and 21 χ_{ij} in Eq. (2). We obtain these parameters from 27 fundamentals, first overtones, and combination bands. Assignments on the basis of Eq. (2) are not possible when a variational level is not close to one of the levels of Eq. (2) or when two variational levels are close to the same level of Eq. (2). This is sometimes the case for variational levels higher than about 5000 cm^{-1} above the zero-point energy (ZPE). To deal with this problem, we would need to extend the model of Eq. (2) by adding Darling-Dennison and Fermi resonance terms to an effective Hamiltonian. We do not take this approach since the simple model of Eq. (2) works for assigning vibrational levels up to about 6000 cm^{-1} .

In the ro-vibrational case, vibrational energy level spacings are generally large enough and coupling is generally small enough that, for J values up to $J = 5$, $2J + 1$ rotational levels can be associated with each of the vibrational levels. $J_{K_a K_c}$ labels were assigned to ro-vibrational levels with $J \leq 5$ by comparing them to rigid-rotor energy levels, obtained by diagonalizing a $(2J + 1) \times (2J + 1)$ Hamiltonian matrix, of an asymmetric top with the rotational constants A, B , and C determined, for each vibrational state, from the $J = 1$ levels.

B. CH_2D^+

We calculated CH_2D^+ levels using 10 PODVR functions for each of the radial coordinates and maximum l (l_{max}) and m (m_{max}) spherical harmonic values in the bend-rotation basis of 30. The $J = 0$ levels differ by less than 0.01 cm^{-1} , and in most cases less than 0.001 cm^{-1} , up to about

6000 cm^{-1} above the zero-point energy, from levels computed with 10 PODVR functions and $l_{\max} = m_{\max} = 32$ and with 12 PODVR functions and $l_{\max} = m_{\max} = 30$. The final CH_2D^+ basis had approximately 10.4 million even-parity and 9.5 million odd-parity basis functions.

1. *Energies and Labels for $J=0$ States*

Vibrational levels of CH_2D^+ up to about 6000 cm^{-1} with symmetry labels are shown in Table 1. By comparing with experimental levels in Ref. [17], it is easy to assign normal mode labels to the fundamentals since they are well separated from overtones and combinations. The fundamental vibrations from Table 1 of Ref. [17] are ν_1 (symmetric C-H stretch), ν_2 (C-D stretch), ν_3 (in-plane C-H bend), ν_4 (out-of-plane bend), ν_5 (asymmetric C-H stretch), ν_6 (in-plane C-D bend).

For CH_2D^+ there are precise experimental values for the vibrational frequencies only for the fundamental CH symmetric and asymmetric stretching modes^{11,14,16}. However, Asvany et al. have recently reported low-resolution experimental frequencies for the remaining fundamentals, using an LIR technique, enabling a more comprehensive comparison¹⁷. In addition, Cunha de Miranda et al. calculate the fundamentals with a vibrational configuration interaction (VCI) method developed by Rauhut^{13,51}. They use normal coordinates and an N-mode representation of their own PES and the reciprocal inertia tensor that is truncated at the three-modes^{52,53}. They assume that because four-mode terms are less important for CH_3^+ , they will also be less important for CH_2D^+ and CD_2H^+ .

Fundamental energies reported in the papers cited above and those calculated in this work are listed in Table 2. Agreement of our calculated levels with all of the previously reported levels is good for all but the bending modes. Our stretch fundamentals agree well with the high resolution values. Our bending fundamentals are between 10 to 20 cm^{-1} lower than the experimental values. This is due to the scaling of the angular coordinates in the YS PES. For the radial coordinates, as Cunha de Miranda et al. discuss, the angular scale factor, 0.96445, is too small and shifts down all bending levels¹³. For the stretch states, our levels appear about as close to their experimental counterparts as those calculated by Ref. [13].

TABLE 1. Low-lying CH_2D^+ vibrational levels (in cm^{-1}) relative to the ZPE (6172.386 cm^{-1})

A+		B+		A-		B-	
ν_3	1379.257	ν_6	1158.980	$\nu_4 + \nu_6$	2447.846	ν_4	1283.324
ν_2	2236.034	$\nu_6 + \nu_3$	2535.445	$\nu_3 + \nu_4 + \nu_6$	3831.259	$\nu_3 + \nu_4$	2669.155
$2\nu_6$	2324.759	ν_5	3103.438	$\nu_4 + \nu_5$	4370.325	$\nu_2 + \nu_4$	3510.184
$2\nu_4$	2560.587	$\nu_6 + \nu_2$	3390.614	$\nu_2 + \nu_4 + \nu_6$	4670.790	$\nu_4 + 2\nu_6$	3617.923
$2\nu_3$	2752.210	$3\nu_6$	3497.851	$\nu_4 + 3\nu_6$	4794.315	$3\nu_4$	3832.352
ν_1	3005.774	$2\nu_4 + \nu_6$	3731.010	$3\nu_4 + \nu_6$	5009.350	$2\nu_3 + \nu_4$	4050.169
$\nu_2 + \nu_3$	3614.217	$2\nu_3 + \nu_6$	3905.632	$2\nu_3 + \nu_4 + \nu_6$	5210.116	$\nu_1 + \nu_4$	4282.260
$\nu_3 + 2\nu_6$	3698.835	$\nu_1 + \nu_6$	4157.228	$\nu_1 + \nu_4 + \nu_6$	5439.339	$\nu_2 + \nu_3 + \nu_4$	4895.165
$\nu_3 + 2\nu_4$	3950.481	$\nu_3 + \nu_5$	4480.927	$\nu_3 + \nu_4 + \nu_5$	5754.159	$\nu_3 + \nu_4 + 2\nu_6$	4999.035
$3\nu_3$	4120.544	$\nu_2 + \nu_3 + \nu_6$	4764.737			$\nu_3 + 3\nu_4$	5225.047
$\nu_5 + \nu_6$	4272.969	$\nu_3 + 3\nu_6$	4869.483			$3\nu_3 + \nu_4$	5428.451
$\nu_1 + \nu_3$	4416.194	$\nu_3 + 2\nu_4$	5118.393			$\nu_4 + \nu_5 + \nu_6$	5545.231
$2\nu_2$	4426.597	$3\nu_3 + \nu_6$	5271.361			$2\nu_2 + \nu_4$	5690.358
$\nu_2 + 2\nu_6$	4546.581	$\nu_5 + \nu_2$	5337.022			$\nu_1 + \nu_3 + \nu_4$	5699.330
$4\nu_6$	4677.309	$\nu_5 + 2\nu_6$	5449.054			$\nu_2 + \nu_4 + 2\nu_6$	5831.756
$\nu_2 + 2\nu_4$	4777.841	$\nu_1 + \nu_3 + \nu_6$	5564.597			$\nu_4 + 4\nu_6$	5976.375
$2\nu_4 + 2\nu_6$	4905.676	$2\nu_2 + \nu_6$	5585.491				
$\nu_2 + 2\nu_3$	4986.011	$2\nu_4 + \nu_5$	5631.562				
$2\nu_2 + 2\nu_6$	5066.852	$\nu_2 + 3\nu_6$	5707.818				
$4\nu_4$	5098.974	$2\nu_3 + \nu_5$	5847.596				
$\nu_1 + \nu_2$	5233.391	$5\nu_6$	5862.306				
$\nu_1 + 2\nu_6$	5317.323	$\nu_2 + 2\nu_4 + \nu_6$	5944.933				
$2\nu_3 + 2\nu_4$	5335.398						
$4\nu_3$	5485.501						
$\nu_1 + 2\nu_4$	5552.525						
$\nu_3 + \nu_5 + \nu_6$	5647.309						
$2\nu_2 + \nu_3$	5803.041						
$\nu_1 + 2\nu_3$	5810.416						
$\nu_2 + \nu_3 + 2\nu_6$	5917.232						

2. Energies and Labels for $J>0$ Ground, ν_1 , and ν_5 States

Calculated and experimental ro-vibrational levels of CH_2D^+ are listed in Tables 3, 4, and 5, for the ground, ν_1 , and ν_5 states respectively. The experimental levels were calculated using the best-fit molecular parameters of Table 4 in Ref. [14]. There is excellent agreement for all 3 bands.

TABLE 2. Experimental and calculated CH_2D^+ fundamental modes (in cm^{-1}).

Fundamental Mode	Experimental	VCI [13]	This Work
ν_5 : asym. CH stretch	3105.840584(52) ¹⁴	3107	3103.438
ν_1 : sym. CH stretch	3004.764593(75) ¹⁴	3002	3005.774
ν_2 : CD stretch	2236 ¹⁷	2240	2236.034
ν_3 : in-plane CH bend	1385 ¹⁷	1389	1379.257
ν_4 : out-of-plane bend	1305 ¹⁷	1308	1283.324
ν_6 : in-plane C-D bend	1168 ¹⁷	1171	1158.980

The root-mean-square error (RMSE) is similar for the three bands. The average RMSE is 0.08 cm^{-1} .

TABLE 3. Calculated and observed $J < 6$ rotational levels (in cm^{-1}) for the ground state of CH_2D^+ relative to the band origin. Observed levels are obtained from fitted constants in Table 4 of Ref. [14]

Sym.	J_{K_a, K_c}	ν_{calc}	ν_{obs}	$ \nu_{calc} - \nu_{obs} $	Sym.	J_{K_a, K_c}	ν_{calc}	ν_{obs}	$ \nu_{calc} - \nu_{obs} $
A+	0 ₀₀	0.0	-	-	B-	4 ₁₃	106.034	106.139	0.105
A-	1 ₀₁	9.284	9.296	0.012	A-	4 ₂₃	111.065	111.158	0.093
B-	1 ₁₁	12.887	12.893	0.006	A+	4 ₂₂	119.436	119.531	0.095
B+	1 ₁₀	15.132	15.137	0.005	B+	4 ₃₂	136.806	136.872	0.066
A+	2 ₀₂	27.083	27.118	0.035	B-	4 ₃₁	137.941	138.008	0.067
B+	2 ₁₂	29.208	29.238	0.030	A-	4 ₄₁	168.840	168.865	0.025
B-	2 ₁₁	35.940	35.968	0.028	A+	4 ₄₀	168.873	168.898	0.025
A-	2 ₂₁	46.742	46.753	0.011	A-	5 ₀₅	123.335	123.510	0.175
A+	2 ₂₀	47.510	47.521	0.012	B-	5 ₁₅	123.454	123.628	0.175
A-	3 ₀₃	52.308	52.377	0.069	B+	5 ₁₄	153.165	153.324	0.159
B-	3 ₁₃	53.267	53.334	0.066	A+	5 ₂₄	155.747	155.899	0.151
B+	3 ₁₂	66.549	66.611	0.061	A-	5 ₂₃	171.296	171.448	0.152
A+	3 ₂₂	74.575	74.622	0.047	B-	5 ₃₃	184.467	184.592	0.125
A-	3 ₂₁	77.959	78.007	0.048	B+	5 ₃₂	188.343	188.473	0.130
B-	3 ₃₁	98.584	98.602	0.017	A+	5 ₄₂	216.811	216.897	0.086
B+	3 ₃₀	98.760	98.777	0.018	A-	5 ₄₁	217.092	217.178	0.087
A+	4 ₀₄	84.396	84.512	0.116	B-	5 ₅₁	257.616	257.648	0.032
B+	4 ₁₄	84.754	84.869	0.115	B+	5 ₅₀	257.621	257.653	0.032

TABLE 4. Calculated and observed $J < 6$ rotational levels (in cm^{-1}) for the ν_1 state of CH_2D^+ relative to the band origin. Observed levels are obtained from fitted constants in Table 4 of Ref. [14]

Sym.	J_{K_a, K_c}	ν_{calc}	ν_{obs}	$ \nu_{calc} - \nu_{obs} $
A+	0 ₀₀	3005.774	3004.764593(75)	1.009
A-	1 ₀₁	9.241	9.251	0.010
B-	1 ₁₁	12.705	12.705	0.000
B+	1 ₁₀	14.966	14.966	0.001
A+	2 ₀₂	26.920	26.950	0.030
B+	2 ₁₂	28.921	28.942	0.021
B-	2 ₁₁	35.703	35.723	0.020
A-	2 ₂₁	46.090	46.078	0.012
A+	2 ₂₀	46.889	46.878	0.011
A-	3 ₀₃	51.931	51.989	0.058
B-	3 ₁₃	52.808	52.861	0.053
B+	3 ₁₂	66.176	66.225	0.048
A+	3 ₂₂	73.791	73.811	0.019
A-	3 ₂₁	77.290	77.313	0.024
B-	3 ₃₁	97.168	97.133	0.035
B+	3 ₃₀	97.358	97.323	0.035
A+	4 ₀₄	83.733	83.829	0.097
B+	4 ₁₄	84.050	84.145	0.095
B-	4 ₁₃	105.413	105.497	0.084
A-	4 ₂₃	110.080	110.140	0.060
A+	4 ₂₂	118.673	118.740	0.067
B+	4 ₃₂	135.252	135.260	0.009
B-	4 ₃₁	136.470	136.483	0.013
A-	4 ₄₁	166.357	166.285	0.072
A+	4 ₄₀	166.394	166.322	0.072
A-	5 ₀₅	122.331	122.479	0.148
B-	5 ₁₅	122.434	122.580	0.147
B+	5 ₁₄	152.154	152.279	0.125
A+	5 ₂₄	154.477	154.587	0.109
A-	5 ₂₃	170.341	170.456	0.115
B-	5 ₃₃	182.717	182.779	0.062
B+	5 ₃₂	186.835	186.908	0.073
A+	5 ₄₂	214.176	214.163	0.013
A-	5 ₄₁	214.490	214.479	0.012
B-	5 ₅₁	253.768	253.647	0.121
B+	5 ₅₀	253.775	253.654	0.121

TABLE 5. Calculated and observed $J < 6$ rotational levels (in cm^{-1}) for the ν_5 state of CH_2D^+ relative to the band origin. Observed levels are obtained from fitted constants in Table 4 of Ref. [14]

Sym.	J_{K_a, K_c}	ν_{calc}	ν_{obs}	$ \nu_{calc} - \nu_{obs} $
B+	0 ₀₀	3103.438	3105.840584(52)	2.402
B-	1 ₀₁	9.226	9.235	0.009
A-	1 ₁₁	12.765	12.773	0.008
A+	1 ₁₀	14.994	15.000	0.007
B+	2 ₀₂	26.907	26.935	0.028
A+	2 ₁₂	28.985	29.012	0.027
A-	2 ₁₁	35.668	35.692	0.024
B-	2 ₂₁	46.280	46.299	0.019
B+	2 ₂₀	47.047	47.066	0.019
B-	3 ₀₃	51.961	52.017	0.056
A-	3 ₁₃	52.893	52.948	0.055
A+	3 ₁₂	66.075	66.126	0.051
B+	3 ₂₂	73.938	73.984	0.047
B-	3 ₂₁	77.316	77.362	0.046
A-	3 ₃₁	97.589	97.625	0.036
A+	3 ₃₀	97.766	97.802	0.036
B+	4 ₀₄	83.835	83.929	0.094
A+	4 ₁₄	84.181	84.274	0.094
A-	4 ₁₃	105.288	105.374	0.086
B-	4 ₂₃	110.193	110.276	0.083
B+	4 ₂₂	118.538	118.619	0.081
A+	4 ₃₂	135.577	135.648	0.072
A-	4 ₃₁	136.719	136.791	0.071
B-	4 ₄₁	167.112	167.169	0.057
B+	4 ₄₀	167.145	167.202	0.057
B-	5 ₀₅	122.520	122.662	0.142
A-	5 ₁₅	122.634	122.776	0.142
A+	5 ₁₄	152.082	152.213	0.131
B+	5 ₂₄	154.584	154.713	0.130
B-	5 ₂₃	170.062	170.187	0.124
A-	5 ₃₃	182.940	183.057	0.117
A+	5 ₃₂	186.835	186.950	0.115
B+	5 ₄₂	214.796	214.897	0.101
B-	5 ₄₁	215.081	215.182	0.101
A-	5 ₅₁	254.955	255.037	0.081
A+	5 ₅₀	254.961	255.042	0.081

C. CHD_2^+

We calculated CHD_2^+ levels using 10 PODVR functions for each of the radial coordinates and maximum values of l and m that are 36. The $J=0$ levels are converged, with respect to calculations with larger bases, to within 0.01 cm^{-1} , and in most cases within 0.001 cm^{-1} , up to about 6000 cm^{-1} above the zero-point energy. There are about 17.6 million even-parity and 16.2 million odd-parity basis functions.

1. *Energies and Labels for $J=0$ States*

Our calculated and assigned CHD_2^+ vibrational levels up to about 6000 cm^{-1} are shown in Table 6. We report more odd parity states because they are easier to assign owing to the fact that the density of the odd-parity states is lower. The normal modes, from Table 1 of Ref. [17], are ν_1 (C-H stretch), ν_2 (symmetric C-D stretch), ν_3 (in-plane C-D bend), ν_4 (out-of-plane bend), ν_5 (asymmetric C-D stretch), ν_6 (in-plane C-H bend). Assignment of the fundamental levels was straightforward for all but the ν_1 band. Both ν_1 and $3\nu_3$ have A+ symmetry and according to Eq. (2) both have similar energies.

To determine whether 3057.503 cm^{-1} or 3047.170 cm^{-1} should be labelled ν_1 , we compared the computed rotational levels of the two bands with the experimental levels assigned to the ν_1 band and observed that the band centred at 3057.503 cm^{-1} matches better. Further confirmation of this assignment is obtained by examining probability density (PD) plots of the two vibrational wavefunctions. Wavefunctions are computed from eigenvectors obtained using the Lanczos algorithm^{54,55}. The PDs are shown in Figure 2. The PDs at the bottom are obtained from the corresponding wavefunctions by integrating over all coordinates except θ_1 and θ_2 . The PDs at the top are obtained from the corresponding wavefunctions by integrating over all coordinates except r_0 . It is clear that the state on the left has no nodes along r_0 and three nodes along $\theta_1 + \theta_2$, and that the state on the right has no nodes along $\theta_1 + \theta_2$, and a clear node along r_0 . $\theta_1 + \theta_2$ corresponds to the C-D bending normal coordinate. A single node in the r_0 stretch coordinate is visible for the 3057.503 cm^{-1} state, implying that it is ν_1 and three nodes are visible in the $\theta_1 + \theta_2$ bend coordinates for the 3047.170 cm^{-1} state, implying that it is the $3\nu_3$ in-plane C-D bend overtone, which supports the assignment made on the basis of the agreement with the experimental ro-vibrational levels.

TABLE 6. Low-lying CHD_2^+ vibrational levels (in cm^{-1}) relative to the ZPE (5587.511 cm^{-1})

A+		B+		A-		B-	
ν_3	1022.766	ν_6	1267.229	$\nu_4 + \nu_6$	2454.793	ν_4	1181.488
$2\nu_3$	2038.373	$\nu_3 + \nu_6$	2283.408	$\nu_3 + \nu_4 + \nu_6$	3471.129	$\nu_3 + \nu_4$	2207.437
ν_2	2163.478	ν_5	2348.551	$\nu_4 + \nu_5$	3523.910	$2\nu_3 + \nu_4$	3224.426
$2\nu_4$	2362.283	$2\nu_3 + \nu_6$	3295.007	$2\nu_3 + \nu_4 + \nu_6$	4484.001	$\nu_2 + \nu_4$	3332.630
$2\nu_6$	2529.862	$\nu_3 + \nu_5$	3370.728	$\nu_3 + \nu_4 + \nu_5$	4548.546	$3\nu_4$	3542.060
$3\nu_3$	3047.170	$\nu_2 + \nu_6$	3432.313	$\nu_2 + \nu_4 + \nu_6$	4608.436	$\nu_4 + 2\nu_6$	3724.742
ν_1	3057.503	$2\nu_4 + \nu_6$	3639.565	$3\nu_4 + \nu_6$	4822.045	$\nu_1 + \nu_4$	4222.498
$\nu_2 + \nu_3$	3207.758	$3\nu_6$	3788.436	$\nu_4 + 3\nu_6$	4992.257	$3\nu_3 + \nu_4$	4237.907
$\nu_3 + 2\nu_4$	3391.618	$3\nu_3 + \nu_6$	4301.192	$3\nu_3 + \nu_4 + \nu_6$	5489.949	$\nu_2 + \nu_3 + \nu_4$	4381.817
$\nu_3 + 2\nu_6$	3542.622	$\nu_1 + \nu_6$	4333.339	$\nu_1 + \nu_4 + \nu_6$	5507.796	$\nu_3 + 3\nu_4$	4574.928
$\nu_5 + \nu_6$	3629.700	$2\nu_3 + \nu_5$	4384.739	$2\nu_3 + \nu_4 + \nu_5$	5563.576	$\nu_3 + \nu_4 + 2\nu_6$	4737.188
$4\nu_3$	4053.600	$\nu_2 + \nu_3 + \nu_6$	4440.707	$\nu_2 + \nu_3 + \nu_4 + \nu_6$	5607.633	$\nu_4 + \nu_5 + \nu_6$	4811.295
$\nu_1 + \nu_3$	4081.706	$\nu_2 + \nu_5$	4495.301	$\nu_2 + \nu_4 + \nu_5$	5672.240	$4\nu_3 + \nu_4$	5238.670
$\nu_2 + 2\nu_3$	4230.525	$\nu_3 + 2\nu_4 + \nu_6$	4654.275	$\nu_3 + 3\nu_4 + \nu_6$	5832.497	$\nu_1 + \nu_3 + \nu_4$	5256.234
$2\nu_2$	4311.805	$2\nu_4 + \nu_5$	4699.579	$3\nu_4 + \nu_5$	5876.332	$\nu_2 + 2\nu_3 + \nu_4$	5400.157
$2\nu_3 + 2\nu_4$	4409.381	$\nu_3 + \nu_6$	4798.859	$\nu_3 + \nu_4 + 3\nu_6$	6002.189	$2\nu_2 + \nu_4$	5476.032
$\nu_2 + 2\nu_4$	4501.989	$\nu_5 + 2\nu_6$	4904.576	$\nu_4 + \nu_5 + 2\nu_6$	6093.268	$2\nu_3 + 3\nu_4$	5592.336
$2\nu_3 + 2\nu_6$	4550.266					$\nu_2 + 3\nu_4$	5671.742
$\nu_3 + \nu_5 + \nu_6$	4626.711					$2\nu_3 + \nu_4 + 2\nu_6$	5744.223
$2\nu_5$	4674.210					$\nu_3 + \nu_4 + \nu_5 + \nu_6$	5801.073
$\nu_2 + 2\nu_6$	4701.527					$\nu_4 + 2\nu_5$	5849.420
$4\nu_4$	4720.538					$\nu_2 + \nu_4 + 2\nu_6$	5885.018
$2\nu_4 + 2\nu_6$	4913.518					$5\nu_4$	5897.473
$4\nu_6$	5043.717					$3\nu_4 + 2\nu_6$	6098.691

TABLE 7. Experimental and calculated CHD_2^+ fundamental modes (in cm^{-1})

Fundamental Mode		Experimental	VCI [13]	This Work
ν_1 :	CH stretch	3056.177571(1) ¹⁶	3055	3057.503
ν_5 :	asym. CD stretch	2346 ¹⁷	2356	2348.551
ν_2 :	sym. CD stretch	2165 ¹⁷	2168	2163.478
ν_6 :	in-plane CH bend	1276 ¹⁷	1281	1267.229
ν_4 :	out-of-plane bend	1200 ¹⁷	1205	1181.488
ν_3 :	in-plane C-D bend	1034 ¹⁷	1036	1022.766

FIG. 2. CHD_2^+ probability density plots for the 3047.170 cm^{-1} state along r_0 stretch (upper-left), 3057.503 cm^{-1} state along r_0 stretch (upper-right), 3047.170 cm^{-1} state $\theta_1 + \theta_2$ bend (lower-left), and 3057.503 cm^{-1} state $\theta_1 + \theta_2$ bend (lower-right)

We compare our CHD_2^+ fundamentals with those previously reported in Table 7. There is high-resolution data available only for ν_1 ¹⁶. The experimental fundamentals of Asvany et al.¹⁷, the VCI fundamentals of Cunha de Miranda et al.¹³, and our fundamentals are listed in Table 7. Similar to CH_2D^+ , our stretching modes appear to agree with experimental values as well or better than those of Ref. [13]. Again, our bend levels are between 10 to 20 cm^{-1} lower than those of the experiment, presumably due to the scaling used by Yu and Sears.

2. Energies and Labels for $J>0$ Ground, ν_1 , and $3\nu_3$ States

Our calculated rotational levels of the ground state of CHD_2^+ are listed in Table 8 and compared to values computed from the fitted parameters from Table 5 of Ref. [16]. The RMSE is 0.09 cm^{-1} , which is consistent with that of the three bands investigated for CH_2D^+ . We do not compare our

computed levels for the ν_1 state with levels obtained from a fitting Hamiltonian. In Ref. [16], the authors had trouble fitting the ν_1 state and did not report parameters. Ref. [11] did report parameters and we could use them to compute levels, but we prefer to determine experimental rotational levels by combining the ground state rotational levels obtained from constants in Table 5 of Ref. [16] with the ro-vibrational transitions in their Table 1. They are reported in the $\nu_{1,obs}$ column of Table 9. Using these "observed" levels, the RMSE is slightly larger than 0.5 cm^{-1} , i.e., significantly higher than it is for the ground state, the only state for which fitted parameters are available. We attribute the larger RMSE to the PES. If vibrational energy levels are close, then small changes in the PES used to compute them may shift the levels considerably.

The larger RMSE is consistent with the findings of Jagod et al.¹¹ who discovered that the ν_1 band is significantly perturbed. The perturbation was confirmed in a recent report by Jusko et al.¹⁶, who propose that the neighbouring $\nu_2 + \nu_3$ and $3\nu_3$ bands, with the same symmetry and similar energies might generate a Fermi resonance. Based on our calculation, the ν_1 state is approximately 150 cm^{-1} away from the $\nu_2 + \nu_3$ state and 10 cm^{-1} away from the $3\nu_3$ state. We note that although there is a presumed down-shift in the bend fundamentals due to the PES, the $3\nu_3$ band should still be closer to ν_1 than $\nu_2 + \nu_3$, making it a more likely perturber. Since ν_3 is about 11 cm^{-1} lower than the experiment value, the expected errors for $3\nu_3$ and $\nu_2 + \nu_3$ are on the order 33 cm^{-1} and 11 cm^{-1} respectively.

Ref. [16] also reports ro-vibrational transitions that appear not to be associated with ν_1 , presumably due to a perturbing band, probably either $\nu_2 + \nu_3$ or $3\nu_3$. For completeness, in this paper we also report, in Table 9, our calculated rotational levels for both possibilities. In most cases it is straightforward to match up rigid-rotor levels and variational levels and thereby to assign the variational levels. Identifying rotational levels for $\nu_2 + \nu_3$ (3207.758 cm^{-1}) is complicated by the fact that they overlap with rotational levels in the $2\nu_3 + \nu_4$ band at 3224.426 cm^{-1} . At $J = 5$, where rotational levels of the two vibrational states are close, we could not use the rigid-rotor model comparison to clearly assign variational levels. To disentangle the states, we plot reduced energy levels as a function of J . Once rotational levels are attributed to vibrational states, they are assigned $J_{K_a K_c}$ labels assuming the standard rigid-rotor energy level order. In some cases, symmetries of nearly degenerate rotational levels with the same value of K_a or K_c and in the $\nu_2 + \nu_3$ vibrational state, are not the same as in the ground state.

In addition, the G_4 symmetries obtained from the variational ground state rotational levels are linked with the evenness and oddness of K_a and K_c . To understand the relation one can use

"equivalent rotations"⁴⁵. They depend on how the principal axes are oriented with respect to the two identical nuclei. For CH_2D^+ , the C_2 axis is a -axis, as is the case for H_2CO in Table 12-9 of Ref. [45]. The ee, oo, eo, oe (parity of K_a and K_c) levels are A+, B-, A-, B+ respectively. See Table 3. For CHD_2^+ , the C_2 axis is b -axis, as for H_2O , in Table 12-8 of Ref. [45]. The ee, oo, eo, oe levels are A+, A-, B-, B+ respectively. See Table 8.

IV. CONCLUSION

Due to their presumed importance in molecular clouds, there is an ongoing effort to identify CH_2D^+ and CHD_2^+ in interstellar space. To do so it is necessary to have accurate values of ro-vibrational line positions. One way to obtain such values is by doing experiments^{4,10-17}. Another way is to compute them. We use parity-adapted bend-rotation functions and PODVR stretch functions with a polyspherical Hamiltonian in orthogonal coordinates and an iterative eigensolver. The energy levels we obtain agree very well with available experimental data. For stretch bands that have been studied at high resolution, the root mean square errors are less than 1 cm^{-1} . Errors are larger, for both isotopologues, for bend states. We attribute these errors to the potential energy surface. Wavefunction and probability distribution plots are used to make assignments. For both isotopologues, we predict many energy levels in the bands that have already been studied and also in bands that have not yet been observed. For CHD_2^+ , the observed ν_1 band is perturbed.¹⁶ According to our calculations, the $3\nu_3$ state is the most likely perturber.

V. ACKNOWLEDGEMENTS

We are grateful for financial support from the Natural Sciences and Engineering Research Council of Canada and computer time from Compute Canada. We appreciate encouragement from Oskar Asvany.

TABLE 8. Calculated and observed $J < 6$ rotational levels (in cm^{-1}) for the ground state of CHD_2^+ relative to the band origin. Observed levels are obtained from fitted constants in Table 5 of Ref. [16]

Sym.	J_{K_a, K_c}	ν_{calc}	ν_{obs}	$ \nu_{calc} - \nu_{obs} $
A+	0 ₀₀	0.0	-	-
B-	1 ₀₁	7.495	7.506	0.011
A-	1 ₁₁	10.061	10.068	0.007
B+	1 ₁₀	11.934	11.942	0.008
A+	2 ₀₂	21.768	21.799	0.031
B+	2 ₁₂	23.176	23.204	0.028
A-	2 ₁₁	28.795	28.824	0.029
B-	2 ₂₁	36.486	36.505	0.019
A+	2 ₂₀	37.201	37.221	0.020
B-	3 ₀₃	41.882	41.943	0.061
A-	3 ₁₃	42.459	42.518	0.059
B+	3 ₁₂	53.506	53.567	0.061
A+	3 ₂₂	58.964	59.015	0.051
B-	3 ₂₁	62.040	62.094	0.054
A-	3 ₃₁	76.827	76.864	0.037
B+	3 ₃₀	77.012	77.050	0.037
A+	4 ₀₄	67.450	67.551	0.101
B+	4 ₁₄	67.646	67.746	0.100
A-	4 ₁₃	85.181	85.282	0.101
B-	4 ₂₃	88.350	88.443	0.093
A+	4 ₂₂	95.773	95.872	0.099
B+	4 ₃₂	107.824	107.904	0.080
A-	4 ₃₁	108.996	109.079	0.083
B-	4 ₄₁	131.395	131.456	0.060
A+	4 ₄₀	131.435	131.495	0.061
B-	5 ₀₅	98.508	98.658	0.151
A-	5 ₁₅	98.567	98.718	0.151
B+	5 ₁₄	122.752	122.902	0.150
A+	5 ₂₄	124.224	124.369	0.145
B-	5 ₂₃	137.723	137.876	0.153
A-	5 ₃₃	146.394	146.528	0.134
B+	5 ₃₂	150.236	150.378	0.141
A+	5 ₄₂	170.397	170.512	0.115
B-	5 ₄₁	170.729	170.846	0.116
A-	5 ₅₁	200.280	200.372	0.091
B+	5 ₅₀	200.288	200.379	0.091

TABLE 9. Calculated and observed $J < 6$ rotational levels (in cm^{-1}) for the ν_1 band of CHD_2^+ relative to the band origin. The $3\nu_3$ perturbing band is included for comparison. Observed levels are obtained from fitted ground state levels (included in Table 8) and the ro-vibrational transitions in Table 1 of Ref. [16] $J_{K_a K_c}$ labels are assigned by assuming the usual rigid rotor order.

Sym.	$J_{K_a K_c}$	$3\nu_{3,calc}$	$(\nu_2 + \nu_3)_{calc}^a$	$\nu_{1,calc}$	$\nu_{1,obs}$	$ \nu_{1,calc} - \nu_{1,obs} $
A+	0 ₀₀	3047.170	3207.758	3057.503	3056.177571(1)	1.325
B-	1 ₀₁	7.510	7.432	7.474	7.476	0.001
A-	1 ₁₁	9.493	8.541	9.812	9.935	0.123
B+	1 ₁₀	11.496	10.250	11.715	11.823	0.108
A+	2 ₀₂	21.594	21.289	21.610	21.680	0.070
B+	2 ₁₂	22.511	21.611	22.854	22.997	0.143
A-	2 ₁₁	28.515	26.641	28.563	28.658	0.095
B-	2 ₂₁	34.411	30.715	35.626	36.027	0.400
A+	2 ₂₀	35.385	31.789	36.397	36.767	0.370
B-	3 ₀₃	41.234	40.664	41.502	41.663	0.162
A-	3 ₁₃	41.536	40.678	41.993	42.186	0.194
B+	3 ₁₂	53.221	49.910	53.165	53.301	0.136
A+	3 ₂₂	56.935	52.065	58.030	58.447	0.417
B-	3 ₂₁	60.805	56.499	61.304	61.716	0.412
A-	3 ₃₁	72.130	65.271	75.099	75.808	0.708
B+	3 ₃₀	72.474	66.089	75.310	76.028	0.718
A+	4 ₀₄	66.197	65.453 (B+)	66.801	67.061	0.260
B+	4 ₁₄	66.279	65.483 (A+)	66.962	67.233	0.271
A-	4 ₁₃	84.410	77.964	84.528	84.820	0.292
B-	4 ₂₃	86.174	78.642	87.262	87.729	0.467
A+	4 ₂₂	95.005	89.073	95.051	95.350	0.299
B+	4 ₃₂	103.448	94.298	106.031	106.767	0.736
A-	4 ₃₁	105.420	98.155	107.347	108.084	0.737
B-	4 ₄₁	122.813	113.968	128.634	129.539	0.906
A+	4 ₄₀	122.912	114.049	128.680	129.589	0.909
B-	5 ₀₅	96.569	95.806 (A-)	97.558	97.920	0.363
A-	5 ₁₅	96.588	95.824 (B-)	97.605	97.971	0.365
B+	5 ₁₄	120.982	109.925	121.646	122.135	0.489
A+	5 ₂₄	121.619	110.068	122.884	123.440	0.556
B-	5 ₂₃	136.960	127.559	136.821	137.195	0.374
A-	5 ₃₃	142.187	129.605	144.476	145.259	0.782
B+	5 ₃₂	147.896	139.193	148.715	149.379	0.664
A+	5 ₄₂	162.407	152.358	167.553	168.535	0.982
B-	5 ₄₁	163.192	152.963	167.938	168.940	1.001
A-	5 ₅₁	186.551	175.918	196.373	-	-
B+	5 ₅₀	186.577	175.943	196.382	-	-

^a In some cases, due to coupling, the symmetries of nearly degenerate $J_{K_a K_c}$ levels in the $\nu_2 + \nu_3$ vibrational state are not the same as the symmetries of the $J_{K_a K_c}$ levels in the ground state.

REFERENCES

- ¹E. Herbst and W. Klemperer, “The formation and depletion of molecules in dense interstellar clouds,” *The Astrophysical Journal* **185**, 505–534 (1973).
- ²P. R. Bunker, “Allowed transitions of the dipole moment of HD^+ ,” *Chemical Physics Letters* **27**, 322–324 (1974).
- ³P. Jensen, “Calculation of rotation-vibration linestrengths for triatomic molecules using a variational approach: Application to the fundamental bands of CH_2 ,” *Journal of Molecular Spectroscopy* **132**, 322–324 (1988).
- ⁴T. Amano, “Submillimeter-wave spectrum of CH_2D^+ ,” *Astronomy & Astrophysics* **516**, L4 (2010).
- ⁵E. Roueff, B. Parise, and E. Herbst, “Deuterium fractionation in warm dense interstellar clumps,” *Astronomy & Astrophysics* **464**, 245–252 (2007).
- ⁶B. Parise, S. Leurini, P. Schilke, E. Roueff, S. Thorwirth, and D. C. Lis, “Deuterium chemistry in the Orion bar PDR,” *Astronomy & Astrophysics* **508**, 737–749 (2009).
- ⁷O. Asvany, S. Schlemmer, and D. Gerlich, “Deuteration of CH_n^+ ($n=3-5$) in collisions with HD measured in a low-temperature ion trap,” *The Astrophysical Journal* **617**, 685–692 (2004).
- ⁸A. Wooten and B. E. Turner, “A search for interstellar CH_2D^+ ,” in: S. Kwok, S. Sanford (Eds.), *Organic Matter in Space, IUA Symposium* **251**, 33–34 (2008).
- ⁹E. Roueff, M. Gerin, D. C. Lis, A. Wooten, N. Marcelino, J. Cernicharo, and B. Tercero, “ CH_2D^+ , the search for the holy grail,” *The Journal of Physical Chemistry A* **117**, 9959–9984 (2013).
- ¹⁰M. Rösslein, M.-F. Jagod, C. M. Gabrys, and T. Oka, “Laboratory infrared spectra of CH_2D^+ and HCCD^+ and predicted microwave transitions,” *The Astrophysical Journal* **382**, L51–L53 (1991).
- ¹¹M.-F. Jagod, M. Rösslein, C. M. Gabrys, and T. Oka, “Infrared spectroscopy of carbo-ions: The ν_1 and ν_4 bands of CH_2D^+ , and the ν_1 band of CD_2H^{+1} ,” *Journal of Molecular Spectroscopy* **153**, 666–679 (1992).
- ¹²S. Gärtner, J. Krieg, A. Klemann, O. Asvany, S. Brünken, and S. Schlemmer, “Rotational transition of CH_2D^+ determined by high-resolution IR spectroscopy,” *Astronomy & Astrophysics* **513**, L3 (2010).

- ¹³B. K. Cunha de Miranda, C. Alcaraz, M. Elhanine, B. Noller, P. Hemberger, I. Fischer, G. A. Garcia, H. Soldi-Lose, B. Gans, L. A. Vieira Mendes, S. Boyé-Péronne, S. Douin, J. Zabka, and P. Botschwina, “Threshold photoelectron spectroscopy of the methyl radical isotopomers, CH₃, CH₂D, CHD₂ and CD₃: Synergy between vuv synchrotron radiation experiments and explicitly correlated coupled cluster calculations,” *The Journal of Physical Chemistry A* **114**, 4818–4830 (2010).
- ¹⁴S. Gärtner, J. Krieg, A. Klemann, O. Asvany, and S. Schlemmer, “High-resolution spectroscopy of CH₂D⁺ in a cold 22-pole ion trap,” *The Journal of Physical Chemistry A* **117**, 9975–9984 (2013).
- ¹⁵M. Töpfer, P. Jusko, S. Schlemmer, and O. Asvany, “Double resonance rotational spectroscopy of CH₂D⁺,” *Astronomy & Astrophysics* **593**, L11 (2016).
- ¹⁶P. Jusko, A. Stoffels, S. Thorwirth, S. Brünken, S. Schlemmer, and O. Asvany, “High-resolution vibrational and rotational spectroscopy of CD₂H⁺ in a cryogenic ion trap,” *Journal of Molecular Spectroscopy* **332**, 59–66 (2017).
- ¹⁷O. Asvany, S. Thorwirth, B. Redlich, and S. Schlemmer, “Spectroscopy of the low-frequency vibrational modes of CH₃⁺ isotopologues,” *Journal of Molecular Spectroscopy* **347**, 1–6 (2018).
- ¹⁸C. Leforestier, “Grid representation of rotating triatomics,” *The Journal of Chemical Physics* **94**, 6388–6397 (1991).
- ¹⁹C. Leforestier, L. B. Braly, K. Liu, M. J. Elrod, and R. J. Saykally, “Fully coupled six-dimensional calculations of the water dimer vibration-rotation-tunneling states with a split Wigner pseudo spectral approach,” *The Journal of Chemical Physics* **106**, 8527–8544 (1997).
- ²⁰P. Sarkar, N. Poulin, and T. Carrington, “Calculating rovibrational energy levels of a triatomic molecule with a simple Lanczos method,” *The Journal of Chemical Physics* **110**, 10269–10274 (1999).
- ²¹S. Y. Lin and H. Guo, “Exact quantum mechanical calculations of rovibrational energy levels of hydrogen peroxide (HOOH),” *The Journal of Chemical Physics* **119**, 5867–5873 (2003).
- ²²J. M. Bowman, T. Carrington, and H.-D. Meyer, “Variational quantum approaches for computer vibrational energies of polyatomic molecules,” *Molecular Physics* **106**, 2145–2182 (2008).
- ²³J. Brown, X.-G. Wang, R. Dawes, and T. Carrington, “Computational study of the rovibrational spectrum of (OCS)₂,” *The Journal of Chemical Physics* **136**, 134306 (2012).
- ²⁴A. G. Császár, C. Fábri, T. Szidarovszky, E. Mátyus, T. Furtenbacher, and G. Czakó, “The fourth age of quantum chemistry: molecules in motion.” *Physical chemistry chemical physics : PCCP*

- 14**, 1085–1106 (2012).
- ²⁵H.-G. Yu, H. Song, and M. Yang, “A rigorous full-dimensional quantum dynamics study of tunneling splitting of rovibrational states of vinyl radical C_2H_3 ,” *The Journal of Chemical Physics* **146**, 224307 (2017).
- ²⁶H.-G. Yu and T. J. Sears, “Vibrational energy levels of the methyl cation,” *Journal of Chemical Physics* **117**, 666–669 (2002).
- ²⁷X. Chapuisat and C. Jung, “Vector parametrization of the n-body problem in quantum mechanics: Polyspherical coordinates,” *Physical Review A* **45**, 6217–6235 (1992).
- ²⁸M. J. Bramley and T. Carrington, Jr., “A general discrete variable method to calculate vibrational energy levels of three- and four-atom molecules,” *The Journal of Chemical Physics*. **99**, 8519–8541 (1993).
- ²⁹F. Gatti and C. Iung, “Exact and constrained kinetic energy operators for polyatomic molecules: The polyspherical approach,” *Physics Reports* **484**, 1 – 69 (2009).
- ³⁰F. T. Smith, “Modified heliocentric coordinates for particle dynamics,” *Physical Review letters* **45**, 1157–1160 (1980).
- ³¹M. Mladenović, “Rovibrational hamiltonians for general polyatomic molecules in spherical polar parametrization. I. Orthogonal representations,” *The Journal of Chemical Physics* **112**, 1070–1081 (2000).
- ³²P. J. Mohr and B. N. Taylor, “CODATA recommended values of the fundamental physical constants: 1998,” *Reviews of Modern Physics* **72**, 351–495 (2000).
- ³³X.-G. Wang and T. Carrington, Jr., “A finite basis representation Lanczos calculation of the bend energy levels of methane,” *The Journal of Chemical Physics* **118**, 6946–6956 (2003).
- ³⁴X.-G. Wang and T. Carrington Jr., “Contracted basis Lanczos methods for computing numerically exact rovibrational levels of methane,” *The Journal of Chemical Physics* **121**, 2937–2954 (2004).
- ³⁵J. C. Light, I. P. Hamilton, and J. V. Lill, “Generalized discrete variable approximation in quantum mechanics,” *The Journal of Chemical Physics* **82**, 1400–1409 (1985).
- ³⁶J. C. Light and T. Carrington, “Discrete-variable representations and their utilization,” *Advances in Chemical Physics* **114**, 263–310 (2000).
- ³⁷H. Wei and T. Carrington, Jr., “The discrete variable representation of triatomic hamiltonian in bond length-bond angle coordinates,” *The Journal of Chemical Physics* **97**, 3029–3037 (1992).

- ³⁸J. Echave and D. C. Clary, "Potential optimized discrete variable representation," *Chemical Physics Letters* **190**, 225–230 (1992).
- ³⁹R. N. Zare, *Angular Momentum* (John Wiley & Sons, 1988).
- ⁴⁰X.-G. Wang and T. Carrington, Jr., "A symmetry-adapted Lanczos method for calculating energy levels with different symmetries from a single set of coordinates," *Journal of Chemical Physics* **114**, 1473–1477 (2001).
- ⁴¹R. Chen and H. Guo, "A single Lanczos propagation method for calculating transition amplitudes. II. Modified QL and symmetry adaptation," *The Journal of Chemical Physics* **114**, 1467–1472 (2001).
- ⁴²X.-G. Wang and T. Carrington, Jr., "Six-dimensional variational calculation of the bending energy levels of HF trimer and DF trimer," *The Journal of Chemical Physics* **115**, 9781–9796 (2001).
- ⁴³J. K. Cullum and R. A. Willoughby, *Lanczos Algorithms for Large Symmetric Eigenvalue Computations* (Society for Industrial and Applied Mathematics, 2002).
- ⁴⁴X.-G. Wang and T. Carrington, Jr., "Vibrational levels of Ar₄: New odd-parity bosonic states," *The Journal of Physical Chemistry A* **111**, 10220–10225 (2007).
- ⁴⁵P. R. Bunker and P. Jensen, *Molecular Symmetry and Spectroscopy*, 2nd ed. (NRC Research Press, 1998).
- ⁴⁶U. Manthe and H. Köppel, "New method for calculating wave packet dynamics: Strongly coupled surfaces and the adiabatic basis," *The Journal of Chemical Physics* **93**, 345–356 (1990).
- ⁴⁷X.-G. Wang and T. Carrington, Jr., "Improving the calculation of rovibrational spectra of five-atom molecules with three identical atoms by using a C_{3v}(G₆) symmetry-adapted grid: Applied to CH₃D and CHD₃," *The Journal of Chemical Physics* **123**, 154303 (2005).
- ⁴⁸X.-G. Wang, T. Carrington, J. Tang, and A. R. W. McKellar, "Theoretical and experimental studies of the infrared rovibrational spectrum of He₂-N₂O," *The Journal of Chemical Physics* **123**, 034301 (2005).
- ⁴⁹M. J. Bramley, J. W. Tromp, T. Carrington, and G. C. Corey, "Efficient calculation of highly excited vibrational energy levels of floppy molecules: The band origins of H₃⁺ up to 35000 cm⁻¹," *The Journal of Chemical Physics* **100**, 6175–6194 (1994).
- ⁵⁰D. Papoušek and M. R. Aliev, *Molecular Vibrational-Rotational Spectra: theory and applications of high resolution infrared, microwave, and Raman spectroscopy of polyatomic molecules* (Elsevier Scientific Pub. Co., 1982).

- ⁵¹G. Rauhut, "Configuration selection as a route towards efficient vibrational configuration interaction calculations," *The Journal of Chemical Physics* **127**, 184109 (2007).
- ⁵²S. Carter, J. M. Bowman, and N. C. Handy, "Extensions and tests of "Multimode": a code to obtain accurate vibration/rotation energies of many-mode molecules," *Theoretical Chemistry Accounts* **100**, 191–198 (1998).
- ⁵³J. M. Bowman, S. Carter, and X. Huang, "Multimode: A code to calculate rovibrational energies of polyatomic molecules," *International Reviews in Physical Chemistry* **22**, 533–549 (2003).
- ⁵⁴M. J. Bramley and T. Carrington, "Calculation of triatomic vibrational eigenstates: Product or contracted basis sets, Lanczos or conventional eigensolvers? What is the most efficient combination?" *The Journal of Chemical Physics* **101**, 8494–8507 (1994).
- ⁵⁵X.-G. Wang and T. Carrington, "A contracted basis-Lanczos calculation of vibrational levels of methane: Solving the Schrödinger equation in nine dimensions," *The Journal of Chemical Physics* **119**, 101–117 (2003).