$$\langle \vec{R} | \Psi(\tau) \rangle = \sum_i^{N_{\text{walker}}} W_i(\tau) \delta^{3N}(\vec{R} - \vec{R}_i(\tau)) |\Phi_{i,J}(\tau)\rangle$$

1
2
3
4
5
6
7
8
9 Calculating Rovibrationally Excited States of H_2D^+ and
10 HD_2^+ by Combination of Fixed Node and Multi-State
11 Rotational Diffusion Monte Carlo
12
13
14

15
16 Jason E. Ford¹, Anne B. McCoy²

17
18 *Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio*
19 *43210, United States*
20
21
22

23
24 **Abstract**
25

26
27 In this work the efficacy of a combined approach for capturing rovibrational
28 coupling is investigated. Specifically, the multi-state rotational DMC method
29 is used in combination with fixed-node DMC in a study of the rotation vi-
30 bration energy levels of H_2D^+ and HD_2^+ . Analysis of the results of these
31 calculations shows very good agreement between the calculated energies and
32 previously reported values. Where differences are found, they can be at-
33 tributed to Coriolis couplings, which are large in these ions and which are
34 not fully accounted for in this approach.
35
36
37
38
39
40
41

42 *Keywords:* rovibrational excitation, diffusion Monte Carlo, H_2D^+ , HD_2^+
43
44

45
46 *Email address:* abmccoy@uw.edu (Anne B. McCoy)

47
48 ¹Current address: Department of Chemistry, Stanford University, Stanford, CA 94305,
49 United States

50
51 ²Current address: Department of Chemistry, University of Washington, Seattle, WA
52 98195, United States
53
54
55
56
57
58

59 *Preprint submitted to Chemical Physics Letters*

December 13, 2015

1. Introduction

Evaluating rotation-vibration energy levels and wave functions for polyatomic molecules that undergo large amplitude motions provides a significant challenge to many theoretical approaches. When vibrations are small amplitude, perturbation theory provides an attractive alternative, even for highly vibrationally excited states [1, 2]. On the other hand, molecules that undergo large amplitude motions sample broad regions of the potential surface. As such, expansions based on a zero-order reference structure become challenging, and perturbation theory can provide unphysical results. Significant advances have been made for studies of triatomic molecules, including H_3^+ and its deuterated analogues for which accurate rotation/vibration energy levels have been reported [3, 4]. Carrington and co-workers have made a variety of advances that allow for the evaluation of vibrational energy levels and wave functions for larger systems [5, 6] including the highly fluxional CH_5^+ [7]. Recently Fabri *et al* reported energies for rotationally excited states of low-lying vibrational levels of H_5^+ [8]. The multi-configurational time-dependent Hartree approach (MCTDH) has also shown significant promise for studies of this class of molecular systems [9, 10]. Wodraszka and Manthe reported results of MCTDH calculations of energies of CH_5^+ with $J \leq 2$ [11]. A challenge that comes in applying these approaches comes from the fact that the convergence properties can be very sensitive to the choice of coordinates.

Over the past several years, several groups have explored approaches based on diffusion Monte Carlo (DMC) [12, 13] for evaluating either rotational or vibrational excited states of molecules that undergo large amplitude vibrational motions even in their ground states [14, 15, 16, 17]. Systems that we

have studied include CH_5^+ [18], H_5^+ [19, 20], H_3^+ [21, 22, 23] as well as their deuterated analogues. Bowman and co-workers also reported energies for the several excited states of H_5^+ [24] based on DMC studies. Very recently, we extended this work to include torsion/rotation excited states of H_5^+ [20]. In the present study, we explore the application of diffusion Monte Carlo to studies of states in which both rotation and a high frequency vibration are excited. We focus this work on H_2D^+ and HD_2^+ . We choose these ions because the absence of a heavy atom makes these particularly challenging from the stand point of large amplitude motions. The fact that they have only three atoms means that accurate energy levels have been reported [3, 4] and we compare our calculated results to these literature values.

2. Theory

2.1. Multi-State Rotational Diffusion Monte Carlo

The diffusion Monte Carlo (DMC) method derives from the isomorphism between the imaginary time ($\tau = it/\hbar$), time-dependent Schrödinger equation

$$\frac{\partial \Psi}{\partial \tau} = \frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} - V(x)\Psi, \quad (1)$$

and the diffusion equation with an added first-order rate term

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - kC. \quad (2)$$

The algorithm for manipulating this isomorphism was originally described by Anderson in 1975 [12]. In this ansatz, the wave function is expanded in an ensemble of weighted (W_i) $3N$ -dimensional Dirac δ -functions called *walkers*, where N represents the number of atoms in the system. As an extension

to Anderson’s ground state method, an associated rotational state vector is incorporated to calculate the energies of rotationally excited states [22]. For the n th state in the multi-state calculation, the basis is now described as

$$\langle \vec{R} | \Psi^{(n)}(\tau) \rangle_R = \sum_i^{N_{\text{walker}}} W_i^{(n)}(\tau) \delta^{3N}(\vec{R} - \vec{R}_i(\tau)) |\Phi_{i,J}^{(n)}(\tau)\rangle. \quad (3)$$

Here $\vec{R}$ represents the Cartesian coordinates of the atoms, and the subscript R is used to indicate that the integral in Eq. 3 is over the vibrational coordinates. Based on Eq. 3, the vibrational part of the wave function is described by an ensemble of weighted δ -functions. The rotational dependence of the wave function is described by the state vector $|\Phi_{i,J}^{(n)}\rangle$ for each of the rotational states of interest. This state vector is expanded in a symmetrized basis of analytic solutions to the symmetric top rigid rotor Hamiltonian, with coordinate-dependent coefficients and parity $p = \pm 1$ [25]. As such,

$$|\Phi_{i,J}^{(n)}(\tau)\rangle = \sum_{K,p} C_{i,J,K,p}^{(n)}(\tau) |J, K\rangle_p, \quad (4)$$

where

$$|J, K\rangle_p = \frac{1}{\sqrt{2p(1 + \delta_{K,0})}} [|J, K\rangle + p(-1)^K |J, -K\rangle]. \quad (5)$$

In these equations, J represents the total angular momentum of a state and K provides the projection of the angular momentum on the body-fixed z -axis. Because the two molecules of interest in the present study, H_2D^+ and HD_2^+ , are asymmetric tops with asymmetry parameters near zero, there is no obvious preferred quantizing axis for the angular momentum. In both cases, we use the c -axis, which corresponds to the axis that is perpendicular to the plane of the ion.

The split operator approximation to the time-dependent Schrödinger equation,

$$|\Psi^{(n)}(\tau + \delta\tau)\rangle \approx e^{-(\hat{V} - E_{\text{ref}}(\tau))\delta\tau} e^{-\hat{h}_{\text{rot}}\delta\tau} e^{-\hat{T}\delta\tau} |\Psi^{(n)}(\tau)\rangle, \quad (6)$$

is used to propagate the wave function in imaginary time [22]. The kinetic energy operator leads to walker diffusion: the coordinates of the k th atom, determined by the δ -function, are each displaced by a random value determined by a Gaussian distribution with $\sigma = \sqrt{\delta\tau/m_k}$. Here m_k is the mass associated with the k th atom. The coefficients in the expansion of the rotational state vector in Eq. 4 are propagated using the rotational Hamiltonian,

$$\hat{h}_{\text{rot}}(\vec{R}) = \frac{1}{2} \sum_{\alpha,\beta} \hat{J}_\alpha I_{\alpha,\beta}^{-1}(\vec{R}) \hat{J}_\beta, \quad (7)$$

where the $I_{\alpha,\beta}^{-1}$ provide elements of the inverse of the moment of inertia tensor. Coriolis coupling is not explicitly included in this model, and to minimize the magnitude of the Coriolis coupling terms, the moment of inertia tensor is evaluated in an Eckart frame [26, 27]. With this in place, the coefficients of the rotational state vector are updated according to first order time-dependent perturbation theory [22],

$$C_{i,J,K,p}^{(n)}(\tau + \delta\tau) = C_{i,J,K,p}^{(n)}(\tau) - \delta\tau \sum_{K',p} C_{i,J,K',p}^{(n)}(\tau) \langle J, K |_p \hat{h}_{\text{rot}}(\vec{R}_i(\tau + \delta\tau)) | J, K' \rangle_p. \quad (8)$$

After each time-step these coefficients are further adjusted to ensure proper ortho-normalization [22]. Finally, the weight of the i th walker that is associated with the n th rovibrational state, $W_i^{(n)}$, is propagated according to

$$W_i^{(n)}(\tau + \delta\tau) = \exp \left[- (V_i(\tau + \delta\tau) + E_{\text{rot},i}^{(n)}(\tau + \delta\tau) - E_{\text{ref}}^{(n)}(\tau)) \delta\tau \right] W_i^{(n)}(\tau) \quad (9)$$

Here, $E_{\text{rot},i}$ is the average rotational energy,

$$E_{\text{rot},i}^{(n)}(\vec{R}_i(\tau)) = \langle \Phi_{i,J}^{(n)}(\tau) | \hat{h}_{\text{rot}}(\vec{R}_i(\tau)) | \Phi_{i,J}^{(n)}(\tau) \rangle, \quad (10)$$

and V represents the value of the potential at the coordinates of the walker [12]. The energy is shifted by a reference energy,

$$E_{\text{ref}}^{(n)}(\tau) = \bar{V}^{(n)}(\tau) + \bar{E}_{\text{rot}}^{(n)}(\tau) - \alpha \frac{W_{\text{total}}^{(n)}(\tau) - W_{\text{total}}^{(n)}(0)}{W_{\text{total}}^{(n)}(0)}. \quad (11)$$

The reference energy is independently evaluated for each state, and as such a walker will have a different weight for each of the populated rovibrational states. The first two terms represent the weighted ensemble averaged values of the potential and rotational energies, while the final term is introduced to maintain a constant amplitude for the wave function, which is proportional to the summed weight of the walkers, W_{total} . This term includes an empirically determined coefficient, $\alpha = (2\delta\tau)^{-1}$. Each reference energy, $E_{\text{ref}}^{(n)}$, fluctuates about the energy of the n th ro-vibrational state, while the distribution of walkers approaches the n th state's wave function.

2.2. Fixed-Node Diffusion Monte Carlo

Vibrationally excited states can be calculated with DMC by placing a node in the wave function [28, 29]. Operationally, the node is treated as an infinite potential barrier; when walkers diffuse across the node their weights are reduced to zero. The node can be analytically known in cases of high symmetry, such as the asymmetric stretch of H_2D^+ , or found by slowly moving the node along a coordinate until the energy is equal in all nodal regions [30]. Recrossing corrections must also be taken into account due to finite time

step size. In general, for distance d to a node, the probability of recrossing, P_{recross} , is well defined.

$$P_{\text{recross}} = \exp \left[- \frac{m_{\text{eff}} d(\tau) d(\tau + \delta\tau)}{\delta\tau} \right] \quad (12)$$

If this probability is larger than a pseudorandom number drawn from $(0, 1)$, the walker's weight is reduced to zero [28]. In this study, the asymmetric stretch of H_2D^+ and HD_2^+ has been investigated to determine the efficacy of combining the two aforementioned methodologies. The distance to the node and effective mass for the asymmetric stretch vibration in H_2D^+ are given in by

$$d(\tau) = a(\tau) = \frac{1}{\sqrt{2}} (r_{\text{DH}_1}(\tau) - r_{\text{DH}_2}(\tau)), \quad (13)$$

where

$$m_{\text{eff}} = \frac{m_{\text{D}} m_{\text{H}}}{\sqrt{\left(m_{\text{D}} + m_{\text{H}} (1 - \cos \theta_{\text{HDH}}(\tau)) \right) \left(m_{\text{D}} + m_{\text{H}} (1 - \cos \theta_{\text{HDH}}(\tau + \delta\tau)) \right)}} \quad (14)$$

and $a(\tau)$ represents the value of the asymmetric stretch coordinate at time τ . For the purpose of the remainder of this section, we will focus on H_2D^+ , recognizing that analogous expressions can be obtained for HD_2^+

2.3. Rovibrational Excitation

In order to combine the two methods for evaluating rotationally and vibrationally excited states, a basis of direct products of rotational and vibrational states is used. A potential complicating factor in investigating two vibrational states with different symmetries comes from the fact that there are terms in the rotational part of the Hamiltonian that couple the two vibrational states. Specifically, the B_{xy} coefficient in $B_{xy}(\hat{J}_x \hat{J}_y + \hat{J}_y \hat{J}_x)$ is an

odd function of the asymmetric stretch. The fact that $B_{xy}(a) = -B_{xy}(-a)$ presented a challenge for the DMC calculation. To correct for this, walkers were “symmetrized” so that the usual walkers were replaced by

$$\phi_i(\vec{r}_{H_1}, \vec{r}_{H_2}, \vec{r}_D, \tau)_{\pm} = [\phi_i(\vec{r}_{H_1}, \vec{r}_{H_2}, \vec{r}_D, \tau) \pm \phi_i(\vec{r}_{H_2}, \vec{r}_{H_1}, \vec{r}_D, \tau)] / \sqrt{2} \quad (15)$$

where $\phi_i(\vec{r}_{H_1}, \vec{r}_{H_2}, \vec{r}_D, \tau)$ represents a nine-dimensional δ -function at the coordinates of the i th walker at time τ . In Eq. (15), the two hydrogen atoms are labeled such that $a \geq 0$. In cases where the walkers cross the node at $a = 0$, the labels on the two hydrogen atoms were reversed. Weights associated with vibrationally excited states were still reduced to zero when this occurred, but the vibrational ground state retains its weight. It should be noted that although the walkers were “symmetrized” to produce the most accurate calculation, due to the magnitude of the B_{xy} coupling term, the energy correction was well within the error bars. Other terms of the rotational Hamiltonian were unaffected by this symmeterization.

2.4. Computational Details

All DMC calculations were run with $\delta\tau = 5$ au, $\alpha = (2\delta\tau)^{-1}$, and $N_{\text{walker}} = 10\,000$, with an equilibration time of 5 000 au and reference energies averaged over 38 750 au. The reported DMC energies reflect an average of five independent calculations and are provided with 99% confidence intervals. Each calculation included every state, allowing the use of correlated sampling to reduce statistical error of the excited states. Each walker was given an initial weight of 1. In order to maintain a distribution of walkers that each contributed significantly to the wavefunction, low weight walkers were eliminated. This procedure was performed at the end of every time

144 step. If the highest weight associated with the i th walker, $W_{i,\max}$, dropped
 145 below a threshold, W_{thresh} , the walker was replaced. This is accomplished
 146 by copying the coordinates and rotational state vector describing the highest
 147 weight walker to the low weight walker and equally distributing the original
 148 weight between the two. In this study, $W_{\text{thresh}} = N_{\text{walker}}^{-1}$. The geometry of
 149 each walker was initialized to be the equilibrium geometry centered at the
 150 origin with each Cartesian coordinate multiplied by 1.15. The initial rota-
 151 tional state vectors were the eigenstates of the rotational Hamiltonian for the
 152 equilibrium geometry in the principal axis frame. The reference structure for
 153 the Eckart embedding was the equilibrium geometry. The rotational state
 154 vectors were expanded in a basis of direct products of symmetrized solutions
 155 to the symmetric top rigid rotor problem with vibrational ground and first
 156 excited states. The potential energy surface used was constructed by Aguado
 157 and coworkers [31]. Resulting data was primarily compared to spectroscop-
 158 ically accurate variational calculations performed by Miller *et al.* [3] using
 159 the potential energy surface constructed by Meyer *et al* [32].

160 **3. Results and Discussion**

161 The rovibrational energies calculated in this study are reported in Tables
 162 1 and 2 along with previously reported results of variationally calculations
 163 [3, 4]. The zero point energies for both H_2D^+ and HD_2^+ are in excellent
 164 agreement with the reported results of variational calculations [4]. This
 165 demonstrates that the inclusion of several vibrational levels in a single DMC
 166 calculation does not deteriorate the accuracy of the ground state calculation,
 167 although the uncertainties have increased compared to our earlier studies on

168 this system. In studies in which we only evaluated the ground state, the
 169 uncertainties in the energies were smaller than 1.5 cm^{-1} while the deviations
 170 from variational energies were comparable to those reported in Tables 1 and
 171 2 [23]. Likewise, when the multi-state approach was used to evaluate states
 172 of H_2D^+ with $J \leq 3$, the calculated zero-point energy was $3877.0 \pm 2.7 \text{ cm}^{-1}$
 173 [22]. While the uncertainty is larger than for the single state calculation, the
 174 deviation from the corresponding variational energy is much smaller than the
 175 9 cm^{-1} uncertainty reported here.

176 The DMC calculations also agree well with the variational results for states
 177 with either rotational or vibrational excitation, exhibiting differences well
 178 within the statistical error. Further, the calculated energies resulting from
 179 the multi-state method are in good agreement with previous fixed-node cal-
 180 culations. In contrast, the time required to obtain all of the states in Table 1
 181 or Table 2 is comparable to the computer time required to evaluate any one of
 182 these states by the fixed-node approach. The smaller uncertainties reported
 183 for the excited states compared to those for the ground state reflect an added
 184 benefit of the multi-state approach. Because the energies of all of the states
 185 of interest are evaluated in a single calculation, the reported uncertainties
 186 are based on the energy differences obtained from five independent simula-
 187 tions rather than the differences between the absolute energies obtained from the
 188 simulations.

189 The states with excitation in both rotation and vibration exhibit deviations
 190 from the results of the variational calculations that are well outside of the
 191 statistical uncertainties. The differences for states of H_2D^+ are as large as
 192 7.3 cm^{-1} for $J = 1$ and up to 21.4 cm^{-1} for $J = 2$. Similar differences

1
 2
 3
 4
 5
 6
 7
 8
 9 are found for HD_2^+ . One exception is the $|1, 0\rangle_+$ state with $\nu = 1$, where the
 10 energy difference is quite small. This observation provides a clue to the origin
 11 of the errors. When we define the Hamiltonian for the DMC calculations,
 12 we assume that the rotations and vibrations are approximately separable.
 13 The evaluation of the elements of the inverse moment of inertia tensor in
 14 Eq. 7 at the coordinates of each of the walkers allows us to capture the
 15 vibration/rotation couplings that comes through the coordinate dependence
 16 of the rotational constants. In contrast, Coriolis coupling terms that are
 17 proportional to $\hat{p}_i \hat{J}_\alpha$ are not included in our Hamiltonian. These terms couple
 18 rotational levels built off of the first excited states in the asymmetric stretch
 19 and bend. Specifically, the bend fundamentals have frequencies of 2206 or
 20 1968 cm^{-1} for H_2D^+ and HD_2^+ , respectively [33, 3], or roughly 100 cm^{-1} lower
 21 in energy than the asymmetric stretch fundamental. Such couplings will also
 22 be present for the ground vibrational state, but the energy gaps to the lowest
 23 energy vibrationally excited state is more than 1800 cm^{-1} . Based on second
 24 order perturbation theory, the anticipated energy shifts in rotational energies
 25 of the vibrationless level due to Coriolis couplings should be more than an
 26 order of magnitude smaller than for the asymmetric stretch fundamental.
 27 This puts these errors within the uncertainties of the DMC calculations.
 28 In Figures 1 and 2, we plot the energies of the states of H_2D^+ with one
 29 quantum in the asymmetric stretch and the bend for $J = 1$ and 2, respec-
 30 tively. The states are color coded by their symmetry. In the left column, we
 31 plot the previously reported energies obtained from variational calculations
 32 by Miller *et al* [3]. On the right are the energies calculated by DMC, with
 33 the differences in energies given in parentheses. As is seen, the $|1, 0\rangle_+$ state
 34
 35
 36
 37
 38
 39
 40
 41
 42
 43
 44
 45
 46
 47
 48
 49
 50
 51
 52
 53
 54
 55
 56
 57
 58
 59
 60
 61
 62
 63
 64
 65

with one quantum in the asymmetric stretch does not have a corresponding rotational level with one quantum in the bend with the same symmetry. All of the other rotation-vibration levels have at least one state with the same symmetry and J value among the bend fundamentals.

4. Conclusion

In this study, we have explored the feasibility of evaluating rotation and vibration excited states simultaneously. The method generally works very well, although the errors of rotationally excited states are larger for vibrationally excited states than for the vibrationless state. These errors are traced to Coriolis couplings, which will be larger for excited states due to the smaller energy differences among states that can be coupled through this mechanism. While we have identified the source of the errors, the solution is less apparent. Using Eckart embedding to define the body-fixed axis system used to evaluate the elements of the inverse moment of inertia tensor in Eq. 7 reduces the magnitude of the Coriolis couplings, but it does not eliminate them entirely. We further note that H_2D^+ and HD_2^+ represent systems for which the Coriolis couplings will be particularly large due to the small masses of all of the atoms and the high symmetry. Note that in H_3^+ and D_3^+ the asymmetric stretch and bend become degenerate. In molecules with lower symmetry and which include heavy atoms the magnitude of the Coriolis couplings are expected to be considerably smaller.

Acknowledgments

Support of this work by the National Science Foundation through grant CHE-1213347 is gratefully acknowledged. JEF also thanks the College of Arts and Sciences at The Ohio State University for an Undergraduate Research Scholarship.

References

References

- [1] McCoy, A. B.; Burleigh, D. C.; Sibert, E. L. *J. Chem. Phys.* **1991**, *95*, 7449–65.
- [2] Barone, V. *J. Chem. Phys.* **2005**, *122*, 014108/1–10.
- [3] Miller, S.; Tennyson, J.; Sutcliffe, B. T. *Mol. Phys.* **1989**, *66*, 429–456.
- [4] Ramanlal, J.; Polyansky, O. L.; Tennyson, J. *A&A* **2003**, *406*, 383–384.
- [5] Avila, G.; Carrington, T. *J. Chem. Phys.* **2009**, *131*, 174103/1–15.
- [6] Manzhos, S.; Chan, M.; Carrington, T. *J. Chem. Phys.* **2013**, *139*, 051101/1–3.
- [7] Wang, X. G.; Carrington Jr., T. *J. Chem. Phys.* **2008**, *129*, 234102/1–13.
- [8] Fábri, C.; Sarka, J.; Császár, A. G. *J. Chem. Phys.* **2014**, *140*, 051101/1–5.

- 258 [9] Vendrell, O.; Gatti, F.; Meyer, H.-D. *J. Chem. Phys.* **2007**, *127*,
259 184303/1–10.
- 260 [10] Valdès, A.; Prosimiti, R.; Delgado-Barrio, G. *J. Chem. Phys.* **2012**, *137*,
261 214308/1–12.
- 262 [11] Wodraszka, R.; Manthe, U. *The Journal of Physical Chemistry Letters*
263 **2015**, *6*, 4229–4232, PMID: 26538038.
- 264 [12] Anderson, J. B. *J. Chem. Phys.* **1975**, *63*, 1499–1503.
- 265 [13] Suhm, M. A.; Watts, R. O. *Physics Reports* **1991**, *204*, 293–329.
- 266 [14] Moroni, S.; Blinov, N.; Roy, P.-N. *J. Chem. Phys.* **2004**, *121*, 3577–3581.
- 267 [15] Acioli, P. H.; Xie, Z.; Braams, B. J.; Bowman, J. M. *J. Chem. Phys.*
268 **2008**, *128*, 104318/1–6.
- 269 [16] Sebastianelli, F.; Xu, M.; Bačić, Z.; Lawler, R.; Turro, N. J. *J. Am.*
270 *Chem. Soc.* **2010**, *132*, 9826–9832.
- 271 [17] Ramilowski, J. A.; Farrelly, D. *Phys. Chem. Chem. Phys.* **2012**, *14*,
272 8123–8136.
- 273 [18] Johnson, L. M.; McCoy, A. B. *J. Phys. Chem. A* **2006**, *110*, 8213–8220.
- 274 [19] Lin, Z.; McCoy, A. B. *J. Phys. Chem. A* **2013**, *117*, 11725–11736.
- 275 [20] Marlett, M. L.; Lin, Z.; McCoy, A. B. *J. Phys. Chem A* **2015**, *119*,
276 9405–9413.

- [21] Petit, A. S.; Wellen, B. A.; McCoy, A. B. *J. Chem. Phys.* **2013**, *138*, 034105/1–11.
- [22] Petit, A. S.; Ford, J. E.; McCoy, A. B. *J. Phys. Chem. A* **2014**, *118*, 7206–7220.
- [23] Petit, A. S.; McCoy, A. B. *J. Phys. Chem. A* **2013**, *117*, 7009–7018.
- [24] Cheng, T. C.; Bandyopadhyay, B.; Wang, Y.; Carter, S.; Braams, B. J.; Bowman, J. M.; Duncan, M. A. *J. Phys. Chem. Lett.* **2010**, *1*, 758–762.
- [25] Huber, D. *Int. J. Quantum Chem.* **1985**, *28*, 245–267.
- [26] Wilson, E. B.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; Dover: New York, 1955.
- [27] Louck, J. D.; Galbraith, H. W. *Rev. Mod. Phys.* **1976**, *48*, 69–106.
- [28] Anderson, J. B. *J. Chem. Phys.* **1976**, *65*, 4121–4127.
- [29] Reynolds, P. J. *J. Chem. Phys.* **1982**, *77*, 5593–5603.
- [30] Lee, H.-S.; Herbert, J. M.; McCoy, A. B. *J. Chem. Phys.* **1999**, *110*, 5481–5484.
- [31] Aguado, A.; Roncero, O.; Tablero, C.; Sanz, C.; Paniagua, M. *J. Chem. Phys.* **2000**, *112*, 1240–1254.
- [32] Meyer, W.; Botschwina, P.; Burton, P. *J. Chem. Phys.* **1986**, *84*, 891–900.
- [33] Fàrník, M.; Davis, S.; Kostin, M. A.; Polyansky, O. L.; Tennyson, J.; Nesbitt, D. J. *J. Chem. Phys.* **2002**, *116*, 6146–6158.

Table 1: Rovibrational Energies (cm^{-1}) for H_2D^+ , reported relative to the zero point energy, energies of states with quanta in both rotation and vibration given relative to $(E_{\text{ZPE}} + E_{\nu=1})$.

State	$\nu = 0$	$\nu = 0$	$\nu = 1$	$\nu = 1$
$ J, K\rangle_p$	$E(\text{Var.})-E(\text{DMC})$	$E(\text{Var.})^a$	$E(\text{Var.})-E(\text{DMC})$	$E(\text{Var.})^b$
$ 0, 0\rangle$	0^c	0^c	2 ± 6	2335.0
$ 1, 1\rangle_+$	0.1 ± 0.3	45.7	5.4 ± 0.4	48.5
$ 1, 1\rangle_-$	0.3 ± 0.2	60.0	5.7 ± 0.7	67.4
$ 1, 0\rangle_+$	0.0 ± 0.2	72.4	0.0 ± 0.7	73.9
$ 2, 2\rangle_+$	0.4 ± 1.1	131.6	17.2 ± 0.9	142.3
$ 2, 2\rangle_-$	0.7 ± 0.5	138.8	19.8 ± 1.2	155.6
$ 2, 1\rangle_+$	-0.2 ± 1.1	175.9	4.4 ± 1.5	177.0
$ 2, 1\rangle_-$	0.2 ± 0.7	218.6	5.3 ± 2.4	233.0
$ 2, 0\rangle_+$	-0.1 ± 0.9	223.8	2.0 ± 2.7	234.1

^a Ref. [4] ^b Ref. [3]. ^c $E_{\text{ZPE}}(\text{DMC}) = 3978 \pm 9 \text{ cm}^{-1}$ and $E_{\text{ZPE}}(\text{Var.}) = 3978.1 \text{ cm}^{-1}$ [4]

Table 2: Rovibrational Energies (cm^{-1}) for HD_2^+ , reported relative to the zero point energy, energies of states with quanta in both rotation and vibration given relative to $(E_{\text{ZPE}} + E_{\nu=1})$.

State	$\nu = 0$	$\nu = 0$	$\nu = 1$	$\nu = 1$
$ J, K\rangle_p$	$E(\text{Var.})-E(\text{DMC})$	$E(\text{Var.})^a$	$E(\text{Var.})-E(\text{DMC})$	$E(\text{Var.})^b$
$ 0, 0\rangle$	0^c	0^c	-3 ± 6	2079.2
$ 1, 1\rangle_+$	0.1 ± 0.4	34.9	4.6 ± 0.2	40.1
$ 1, 1\rangle_-$	0.1 ± 0.3	49.2	3.1 ± 0.3	50.2
$ 1, 0\rangle_+$	-0.1 ± 0.3	58.0	0.1 ± 0.4	57.8
$ 2, 2\rangle_+$	-0.3 ± 1.1	101.7	12.6 ± 1.2	115.4
$ 2, 2\rangle_-$	0.4 ± 0.7	110.2	16.4 ± 0.7	124.1
$ 2, 1\rangle_+$	-0.2 ± 1.2	136.3	7.3 ± 0.9	146.5
$ 2, 1\rangle_-$	-0.2 ± 1.1	179.1	2.1 ± 1.0	176.2
$ 2, 0\rangle_+$	0.2 ± 1.2	182.0	1.4 ± 0.8	179.1

^a Ref. [4] ^b Ref. [3]. ^c $(E_{\text{ZPE}} + E_{\nu=1})$; $E_{\text{ZPE}}(\text{DMC}) = 3563 \pm 6 \text{ cm}^{-1}$ and $E_{\text{ZPE}}(\text{Var.}) = 3561.4 \text{ cm}^{-1}$ [4].

Figure 1: Energy level diagram for H_2D^+ with $J=1$. The right column provides the calculated DMC energies, while those in the left column are from Ref. [3] and [4]. The states are labeled by their symmetry under C_{2v} , as indicated in the inset.

Figure 2: Energy level diagram for H_2D^+ with $J=2$. The right column provides the calculated DMC energies, while those in the left column are from Ref. [3] and [4]. The states are labeled by their symmetry under C_{2v} , as indicated in the inset.

figure 1

figure 2