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Vibrational dynamics of the H_5^+ and its isotopologues from multiconfiguration time-dependent Hartree calculations

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Full-dimensional multiconfiguration time-dependent Hartree (MCTDH) computations are reported for the vibrational states of the H_5^+ and its H_4D^+ , H_3D_2^+ , H_2D_3^+ , HD_4^+ , D_5^+ isotopologues employing two recent analytical potential energy surfaces of Xie *et al.* [J. Chem. Phys. **122**, 224307 (2005)] and Aguado *et al.* [J. Chem. Phys. **133**, 024306 (2010)]. The potential energy operators are constructed using the n -mode representation adapted to a four-combined mode cluster expansion, including up to seven-dimensional grids, chosen adequately to take advantage in representing the MCTDH wavefunction. An error analysis is performed to quantify the convergence of the potential expansion to reproduce the reference surfaces at the energies of interest. An extensive analysis of the vibrational ground state properties of these isotopes and comparison with the reference diffusion Monte Carlo results by Acioli *et al.* [J. Chem. Phys. **128**, 104318 (2008)] are presented. It is found that these systems are highly delocalized, interconverting between equivalent minima through rotation and internal proton transfer motions even at their vibrational ground state. Isotopic substitution affects the zero-point energy and structure, showing preference in the arrangements of the H and D within the mixed clusters, and the most stable conformers of each isotopomer are the ones with the H in the central position. Vibrational excited states are also computed and by comparing the energies and structures predicted from the two surfaces, the effect of the potential topology on them is discussed.

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I. INTRODUCTION

Since the detection of the H_5^+ ion in 1962 by Dawson and Thicker¹ several experimental and theoretical studies have been devoted to investigate its structure and properties.^{2–14} As the smallest system including a proton transfer has been viewed as the prototypical interconversion, modeled by $\text{H}_3^+\text{H}_2 \leftrightarrow \text{H}_2\text{H}_3^+$, and its molecular properties are therefore an important step to understand larger complexes. Moreover, the H_5^+ cation and its deuterated isotopomers are of particular interest in interstellar chemistry reaction mechanisms.^{15–18}

These cations are highly fluxional with its potential surface presenting many equivalent minima separated by low barriers. The global potential minimum has C_{2v} symmetry with the H_2 molecule attached to an elongated H_3^+ core, with $5!=120$ versions of it with respect to all permutations of identical atoms. There are saddle points of D_{2d} symmetry corresponding to the barriers for the internal proton transfer, with the proton occupying the middle position, and thus “hops,” between the two H_2 groups. Also, there are internal rotations through to the C_{2v} symmetry saddle points, corresponding to rotating a H_2 around the C_2 axis of the H_5^+ . The barrier heights for the proton transfer and H_2 rotations are about 60 and 100 cm^{-1} , respectively,⁹ while higher-lying stationary points are also known on its surface.^{6,9} Numerous electronic structure calculations and normal-mode frequencies at different levels of theory have been reported for the H_5^+ .^{8,19,20} However, it is clear that standard zeroth-order methods of its spectro-

scopic analysis are useless, and to understand the vibrations of H_5^+ proper nuclear quantum mechanical treatments to count with anharmonic effects together with an accurate representation of its potential surface at the configuration space of interest should be considered.

Fortunately, great progress has been made in recent years in the construction of potential energy surfaces (PESs) (see Ref. 21 and references therein) for high-dimensional molecular systems.²² In particular, up to date several H_5^+ surfaces are available in the literature,^{10,12,20,23} with each of them based on different theoretical approaches. In particular, various fitting procedures to *ab initio* data using site-site interactions, diatomics-in molecules, triatomic-in-molecules, generalized many-body expansion, and permutationally invariant functional forms for the parameterization of the surface have been reported.^{9,12,23} An interpolation technique has also been employed on a sparse set on data,¹⁰ and even an “on the fly” reliable representation of it based on improved parameterized functionals^{24–26} within the density functional theory framework has been also proposed.²⁰ These surfaces have been used to carry out theoretical studies on vibrational and collisional dynamics, such as diffusion Monte Carlo (DMC),¹³ path-integral Monte Carlo (PIMC),^{27,28} and molecular dynamics¹¹ calculations, excited vibrational state calculations,²⁹ reduced-dimensional spectral simulations of the infrared (IR) photodissociation of H_5^+ and D_5^+ ,^{5,30–33} and rotational ones for different mixed isotopologues,¹⁴ as well as classical trajectory simulations,¹⁰ and reduced seven-dimensional (7D) quantum scattering dynamics ones for deuterated forms of the H_3^+ + H_2 reaction.³⁴

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From the experimental point of view, H_5^+ and its deuterated isotopologues also present a challenge for laboratory observation mainly due to the postulation for their presence, but still not detected, in the interstellar medium.^{15,16,18} Thus, we should mention the earlier vibrational predissociation spectra recorded by Okumura and Lee² near 4000 cm^{-1} and Bae⁴ around 6000 cm^{-1} for the H_5^+ , and the most recent IR spectra by Duncan and co-workers,⁵ in the spectral regions of 2000–4500 cm^{-1} and 1500–3500 cm^{-1} for the H_5^+ and D_5^+ , respectively. This latter study revealed the major role of the shared-proton stretch mode in the assignment of the experimental features.⁵ Unfortunately, no more experimental data are available in the literature, especially for the lower energy regime for H_5^+ and its isotopes, and theoretical investigations could serve to initialize further laboratory studies for these cations.

Therefore, in this paper we present the results of our calculations of the vibrational levels of H_5^+ and its H_4D^+ , H_3D_2^+ , H_2D_3^+ , HD_4^+ , D_5^+ isotopologues employing the two more recent analytical potential energy surfaces. There have been previous attempts to compute vibrational levels including all nine degrees of freedom for these systems. DMC method is a straightforward way for quantum calculations on large systems, but enables one to obtain, with certainty, only the ground vibrational state and wavefunction, and in this vein DMC calculations have been performed to compute the ground state properties of H_5^+ and its isotopes.¹³ Fixed-node DMC and variational MULTIMODE “reaction-path” (MM-RPH) results on few selected vibrational states of H_5^+ and D_5^+ have been also reported,⁵ while just recently several low-lying vibrational excited levels, up to 20, have been determined from multi-configuration time-dependent Hartree (MCTDH) calculations for the H_5^+ cluster.²⁹ These encouraging results motivated us to undertake a complete characterization of low-lying vibrational levels of its heavier deuterated counterparts, aiming to provide information that could contribute to guide future spectral studies (experimental and theoretical), and further to gain insights into the role of the underlying PES on vibrational spectrum of these ions.

The plan of this paper is as follows: in Sec. II, we outline computational details of the MCTDH calculations.^{35–37} We present the coordinate system and the corresponding Hamiltonian operator for the $\text{H}_5^+/\text{D}_5^+$ systems: in Sec. II A, the kinetic energy operator (KEO) is given, and we also discuss here the construction of the potential energy operator and its accuracy. Section II B presents numerical results on the zero-point energies (ZPE) in comparison with previous data available from the DMC calculations and excited vibrational states of the $\text{H}_5^+/\text{D}_5^+$ isotopic species. Special attention was paid on their convergence with respect to the potential representation and the number of configurations of the MCTDH wavefunction. Finally, some concluding remarks constitute Sec. III.

II. COMPUTATIONAL DETAILS

We employed here the Heidelberg MCTDH package^{35–37} to solve the time-dependent Schrödinger equation. The MCTDH method (see Ref. 38 and references therein) ex-

pands the wavefunction in a sum of products, namely, single-particle functions (SPFs), which in principle allow the treatment of more degrees of freedom, maintaining the correlation between them. The SPFs are one- or multidimensional functions of the system coordinates, and are represented by linear combinations of time-dependent primitive basis functions of discrete variable representation (DVR) grids. The calculation of the Hamiltonian matrix elements requires a major part of the computational resources, and hence their evaluation is essential for the performance of the MCTDH. Thus, the Hamiltonian should be expressed as a sum of products of monoparticle operators to ensure efficiency. KEOs are usually of product form, while potential energy ones are not. Below we present the coordinate system used together with the exact KEO for the $\text{H}_5^+/\text{D}_5^+$, and we discuss an adequate representation of the PESs.

A. Coordinate system and Hamiltonian operator

1. Kinetic energy operator

The $\text{H}_5^+/\text{D}_5^+$ cation is described by the four Jacobi vectors ($\vec{R}$, $\vec{r}$, $\vec{R}_1$, and $\vec{R}_2$) shown in Fig. 1. The expression of the KEO in terms of the angular momenta associated to these Jacobi vectors takes the form³⁹

$$\begin{aligned} \hat{T} = & -\frac{\hbar^2}{2\mu_R} \partial_R^2 - \frac{\hbar^2}{2\mu_1} \partial_{R_1}^2 - \frac{\hbar^2}{2\mu_2} \partial_{R_2}^2 - \frac{\hbar^2}{2m} \partial_r^2 \\ & + \left(\frac{1}{2mr^2} + \frac{1}{2\mu_R R^2} \right) \mathbf{l}^2 \\ & + \left(\frac{1}{2\mu_R R^2} + \frac{1}{2\mu_1 R_1^2} \right) \mathbf{L}_1^2 + \left(\frac{1}{2\mu_R R^2} + \frac{1}{2\mu_2 R_2^2} \right) \mathbf{L}_2^2 \\ & + \frac{\mathbf{L}_1 \cdot \mathbf{L}_2}{\mu_R R^2} + \frac{(\mathbf{L}_1 + \mathbf{L}_2) \cdot \mathbf{l}}{\mu_R R^2}, \end{aligned} \quad (1)$$

where $\mathbf{L}$, $\mathbf{l}$, $\mathbf{L}_1$, and $\mathbf{L}_2$ are the angular momenta associated to the vectors $\vec{R}$, $\vec{r}$, $\vec{R}_1$, and $\vec{R}_2$, respectively, and the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{l} + \mathbf{L}_1 + \mathbf{L}_2 = 0$. The reduced masses are $\mu_1 = \frac{m_1 m_2}{m_1 + m_2}$, $\mu_2 = \frac{m_3 m_4}{m_3 + m_4}$, $\mu_R = \frac{\mu_1 \mu_2}{\mu_1 + \mu_2}$, and $m = \frac{\mu_R m_5}{\mu_R + m_5}$ with m_1 , m_2 , m_3 , m_4 , and m_5 being the masses of the H or D atoms labeled in Fig. 1. We use the set of internal coordinates ($R, R_1, R_2, x, y, z, \theta_1, \theta_2, \alpha$) shown in Fig. 1, in parenthesis, to describe the system. The body fixed frame is chosen such that the Z_{BF} axis is parallel to $\vec{R}$, and that $\vec{R}_1$ is parallel to the ZY_{BF} plane (see Fig. 1). Then, the coordinates R , R_1 , and R_2 are the

FIG. 1. Jacobi vectors description and definition of coordinates used in the calculations of the H_5^+ and its isotopologues.

sizes of the vectors $\vec{R}$, $\vec{R}_1$, and $\vec{R}_2$, respectively. x , y , and z are the coordinates of the proton in the BF frame with origin in the center of mass of the $\text{H}_2\text{-H}_2$ system. θ_1 and θ_2 are the angles of $\vec{R}_1$ and $\vec{R}_2$ with the Z_{BF} axis, and α is the azimuthal angle between R_2 and the Y_{BF} axis. The exact KEO expressed in terms of the internal coordinates is given in the Appendix, and can be used along with a direct product of DVR primitive basis set in each of them.

2. Potential energy operator

As we mentioned above, in order to make the MCTDH method efficient, the potential energy operator must be written as a sum of products of single-particle operators. An efficient approach within the MCTDH code³⁵ to obtain the desired product representation of the PES, called POTFIT,⁴³ is limited to systems with at most 6–7 degrees of freedom, and recently a multigrid POTFIT methodology³⁸ has been proposed. As the grid used to describe H_5^+ is too large to be treated with the POTFIT algorithm, an n -mode representation of the potential is used,⁴⁴ adapted to a four-mode combination scheme. Taking into account the coordinates that are strongly coupled between them, the 9 degrees of freedom are combined into four modes q_i according to the following scheme: $q_1 = [z, R]$, $q_2 = [\alpha, x, y]$, $q_3 = [\theta_1, \theta_2]$, $q_4 = [R_1, R_2]$. In this representation, the potential is approximated by

$$\begin{aligned} \tilde{V}(q_1, q_2, q_3, q_4) = & v^{(0)} + \sum_{i=1}^4 v_i^{(1)}(q_i) + \sum_{i<j}^4 v_{ij}^{(2)}(q_i, q_j) \\ & + \sum_{i<j<k}^4 v_{ijk}^{(3)}(q_i, q_j, q_k) \end{aligned} \quad (2)$$

with $v^{(0)}$ being the potential at a reference geometry $\mathbf{a}$ ($V(\mathbf{a})$) and the other terms come by

$$\begin{aligned} v_i^{(1)}(q_i) &= V(q_i, \mathbf{a}^{(i)}) - v^{(0)}, \\ v_{ij}^{(2)}(q_i, q_j) &= V(q_i, q_j, \mathbf{a}^{(i,j)}) - v_i^{(1)}(q_i) - v_j^{(1)}(q_j) - v^{(0)}, \\ v_{ijk}^{(3)}(q_i, q_j, q_k) &= V(q_i, q_j, q_k, \mathbf{a}^{(i,j,k)}) - v_{ij}^{(2)}(q_i, q_j) \\ &\quad - v_{ik}^{(2)}(q_i, q_k) - v_{jk}^{(2)}(q_j, q_k), \\ &\quad - v_i^{(1)}(q_i) - v_j^{(1)}(q_j) - v_k^{(1)}(q_k) - v^{(0)}. \end{aligned}$$

Here, $\mathbf{a}^{(i)}$ represents the reference point $\mathbf{a}$ except for the i th coordinate, while $\mathbf{a}^{(i,j)}$ and $\mathbf{a}^{(i,j,k)}$ represent the reference point $\mathbf{a}$ except for the (i, j) and (i, j, k) coordinates, respectively. The $v^{(1)}$ terms are the intra-mode potentials keeping the coordinates in the other modes at the reference geometry, $v^{(2)}$ terms account for the mode-mode correlations, while the $v^{(3)}$ are the three-mode correlations between the 4 different modes. Here, the n -mode expansion is truncated at the third order, with the fourth one being the exact representation of the PES. We consider an average over two different reference geometries to construct the potential terms enforcing the symmetry properties in the expansion.^{45,46} One corresponding to a saddle point in the z coordinate of D_{2d} symmetry, and the other one being an equivalent position corresponding to geometry with

TABLE I. MAE and rms values (in cm^{-1}) of the expansion terms in the n -mode representation of the PES of Ref. 12 for the indicated number of points up to energy of 9000 cm^{-1} .

No config.	622 086		5 906 109	
	MAE	rms	MAE	rms
$\sum v^{(1)}$	780.6	1067.7	2735.2	4927.5
$\sum v^{(1)} + \sum v^{(2)}$	309.8	568.0	2451.3	7471.5
$\sum v^{(1)} + \sum v^{(2)} + \sum v^{(3)}$	23.2	51.8	183.8	850.6

a change of 180° in α coordinate. The POTFIT program is then used to convert the n -mode terms of the expansion of Eq. (2) in the sum of products of single-particle operators form required by the MCTDH program.

The quality of the n -mode approximation of the PES is investigated by analyzing the error with respect to the original surface (we choose the PES of Ref. 12) at energies and configurations of the interest. In Table I, we list the mean absolute error (MAE) and the root-mean-square (rms) values by increasing the order of the potential expansion for two different sets of configurations. One includes up to $\approx 6 \times 10^6$ geometries covering the whole coordinates range in the present calculations up to potential energies of 9000 cm^{-1} , while another one is restricted to 6×10^5 configurations, which are selected from the previous set by applying a cutoff at 2000 cm^{-1} in each of the three intra-mode $v_i^{(1)}(q_i)$ term, with $i = 1-3$.

In Figure 2, we show the rms values for increasing order of the potential expansion, e.g., $v^{(0)}$, $v^{(1)}$ up to $v^{(3)}$, for the two sets of data as a function of the potential energy. One can see that the error of the n -mode approximation for the larger set of geometries is highly increasing for energies above 2000 cm^{-1} when the first-order terms are included in the series. By adding the $v^{(2)}$ terms we achieved an error of about 600 cm^{-1} , while the expansion up to third-order arises the rms value to 750 cm^{-1} for potential energy values above 5000 cm^{-1} . Thus, by restricting each of the three $v_i^{(1)}$, $i = 1-3$, modes at energies lower than 2000 cm^{-1} we show

FIG. 2. Convergence of the n -mode representation of the PES as a function of the expansion terms and energy for the total (dashed lines) and selected (solid) number of grid points. In parenthesis, the number of points up to the corresponding energy is shown.

TABLE II. Primitive grid parameters: number and type of the DVR basis set, as well as the range covered by the calculations for each coordinate.

Coord.	z	R	α	x,y	$u_{\theta_1}, u_{\theta_2}$	R_1, R_2
Grid range	(A): $[-1.2, 1.2]$	$[3.25, 5.25]$	$[0, 2\pi]$	$[-0.8, 0.8]$	$[-0.6, 0.6]$	$[0.9, 2.2]$
	(B): $[-1.5, 0.9]$					
	(C): $[-1.9, 0.5]$					
	(D): $[-1.2, 1.2]$					
	(E): $[-1.6, 0.8]$					
No/type of DVR basis	15/HO	20/sin	17/exp	11/HO	9/sin	11/HO

that the convergence of the n -mode representation is smooth and the rms error compared to the reference PES is $\approx 50 \text{ cm}^{-1}$ for the higher energy range of interest. Further, we should point out that the cutoff value, applied only to the first-order terms $v_i^{(1)}$, $i = 1-3$ modes, is quite reasonable compared to the excitation energies for each of them, e.g., shared-proton stretching, torsional, and bending modes.

Once the set of coordinates is chosen, we should also define the parameters of the grid for the representation of the Hamiltonian operator. In Table II, we list the grid parameters for each of the nine internal coordinates. As the center of mass of the coordinate system depends on the positions of the isotopic substitution, the grid range values of the z coordinate are affected, and thus the evaluation of the potential matrix. In this way in total 5 different grids, namely, A, B, C, D, and E, are needed to carry out the MCTDH calculations for the mixed isotopic species of H_5^+ . The underlying primitive basis sets are harmonic oscillator, *sine* and exponential DVR functions. The total number of sampling points on the full product grid is 6×10^9 , however, by employing the n -mode cluster expansion up to 3rd order in combination with the four-mode scheme a reduction in the matrix elements of the potential to 3×10^8 data is achieved. The POTFIT algorithm⁴³ is then used to expand the 2nd- and 3rd-order potential terms in the appropriate product form for the MCTDH calculations.

B. Numerical results and discussion

1. Zero-point energy and ground-state properties

The numerical effort for solving the Schrödinger equation within the MCTDH method mainly depends on the number and size of the basis of time-dependent wavefunctions, called SPFs, used to represent the wavefunction. As mentioned above in the present calculations we introduce 4 com-

bined modes, q , and thus the SPFs are depending on 2 and 3 internal degrees of freedom for the q_1 , q_3 , q_4 , and q_2 modes, respectively. The calculation of the ZPE and the ground-state wavefunction is carried out using the improved relaxation method⁴⁷ implemented in the MCTDH code.³⁵ In Table III, we present the convergence of the ZPE values for the H_5^+ , H_4D^+ , HD_4^+ , and D_5^+ from different MCTDH calculations with increasing the number of SPFs per mode and employing two different recent analytical PESs from Refs. 12 and 23. Both surfaces are based on CCSD(T) *ab initio* data, although different basis sets, and completely different parameterization procedures are used for their construction, with rms error of $10-40 \text{ cm}^{-1}$ at the energy range of interest. A more detailed comparison of them will be presented below.

One can see, in Table III, that with 10, 12, 10, and 5 SPFs in each of the q_i ($i = 1-4$) modes we achieved a convergence of less than 0.5 cm^{-1} in the MCTDH calculations for the ZPEs of the indicated isotopes using the two PESs. Additional convergence calculations are performed based on extrapolation schemes proposed recently.^{48,49} The idea is to carry out a reference calculation by employing a small set of SPFs, and in turn by doubling the number of SPFs in each mode independently to calculate the energy difference with respect to the reference one. At the end the sum of all these differences is added to the reference energy to estimate its extrapolated value. In Table IV, we report the results obtained with a half-size set of SPFs compared to the larger one (see Table III). As it can be seen the larger ΔE values are found for the q_3 and q_4 modes summing up to 8.7 cm^{-1} , and if the number of SPFs in these modes is doubled in the same calculation this difference is almost the same (see 6th row of Table IV). Extrapolated ZPE values of 7205.6 cm^{-1} and 5152.2 cm^{-1} are obtained for the H_5^+ and D_5^+ clusters, with deviation of 3.0 and 1.2 cm^{-1} , respectively, with respect to the largest calculation performed (see last line of Table IV). Therefore, for the

TABLE III. Convergence of the ZPE values (in cm^{-1}) with respect to the number of the SPFs for the H_5^+ , H_4D^+ , HD_4^+ , and D_5^+ systems using the two analytical PESs (PES^a/PES^b) in the MCTDH calculations. PES^a from Ref. 23 and PES^b from Ref. 12.

No SPFs/mode	H_5^+	H_4D^+	HD_4^+	D_5^+
(7,7,7,6)	7343.6/7208.9	...	...	5213.0/5153.7
(8,8,8,4)	7241.8/7207.2	...	...	5180.0/5152.8
(8,8,8,5)	7241.2/7206.6	6892.2/6857.4	5564.3/5537.3	5179.6/5152.5
(8,8,8,6)	7241.1/7206.5	6892.0/6857.3	5564.3/5537.3	5179.6/5152.4
(10,10,10,4)	7238.3/7203.9	...	...	5178.5/5151.5
(10,12,10,4)	7237.9/7203.3	6889.2/6854.6	5562.4/5536.0	5178.3/5151.4
(10,12,10,5)	7237.5/7202.6	6888.7/6854.1	5562.0/5535.6	5177.9/5151.0

TABLE IV. Extrapolation of the ZPE values (in cm^{-1}) by increasing the number of the SPFs for each mode for the H_5^+ and D_5^+ systems in the MCTDH calculations using the PES from Ref. 12. ΔE indicates the energy difference with respect to the energy of the reference calculation with the smaller number of SPFs.

No SPFs/mode	H_5^+		D_5^+	
	ZPE	ΔE	ZPE	ΔE
(5,6,5,3)	7216.4	0.0	5158.0	0.0
(10,6,5,3)	7215.4	-0.93	5157.6	-0.47
(5,12,5,3)	7215.2	-1.17	5157.4	-0.67
(5,6,10,3)	7209.9	-6.50	5154.8	-3.21
(5,6,5,6)	7214.2	-2.21	5156.6	-1.49
(5,6,10,6)	7207.6	-8.8	5153.3	-4.70
Extrapolated energy	7205.6	-10.81	5152.20	-5.85
(10,12,10,5)	7202.6		5151.0	

analytical PES by Aguado *et al.*²³ ZPEs of 7237.5, 6888.7, 5562.0, and 5177.9 cm^{-1} are reported here for first time for the H_5^+ , H_4D^+ , HD_4^+ , and D_5^+ clusters. By comparing them with the ones computed using the PES by Xie *et al.*¹² we see that they are lying higher in energy by $\sim 30 \text{ cm}^{-1}$.

After we checked the convergence of the ground state energies with the SPFs, and in order to evaluate the effect of the n -mode expansion of the PES on them, we list in Table V the ZPE values for increasing order of the potential terms using the reference potential of Ref. 12. The MCTDH results for the H_5^+ , H_4D^+ , HD_4^+ , and D_5^+ are shown by considering the potential expansion up to the 1st-, 2nd-, and 3rd-order terms. One can see that by including higher-order terms leads to similar drop of the ZPE values, between 89–46 and 59–42 cm^{-1} for the 2nd-, and 3rd-order expansions, respectively. For reason of comparison the corresponding DMC values available¹³ using the same original PES¹² are also given. One can see that differences of about 6.0 cm^{-1} are obtained for the H_5^+ and H_4D^+ , while for the HD_4^+ and D_5^+ the differences are smaller within the statistical error of the DMC values. These variations include both convergence errors with respect to the basis set used, as well as the ones arising of the n -mode approximation to the PES, with the latter being, in principal, the larger contribution.

Table VI contains the ZPE values for all mixed isotopomers of H_5^+ indicating the position of the D atoms within the cluster, as well as the type of the z-grid used (see Table II), and compare them with previous calculations, that for the moment are available only for the analytical surface by Xie *et al.*¹² In Figure 3, we present a schematic representation

TABLE V. Comparison of the ZPE values of the indicated systems by varying the order of the n -mode representation of the PES, together with the DMC values from Ref. 13 using the same original PES by Xie *et al.*¹²

$\tilde{V}$	H_5^+	H_4D^+	HD_4^+	D_5^+
$\sum v^{(1)}$	7351.1	6967.2	5650.6	5238.8
$\sum v^{(1)} + \sum v^{(2)}$	7261.8	6899.7	5590.3	5193.1
$\sum v^{(1)} + \sum v^{(2)} + \sum v^{(3)}$	7202.6	6854.1	5535.6	5151.0
DMC	7208 $\pm$ 4	6860 $\pm$ 1	5533 $\pm$ 2	5151 $\pm$ 1

TABLE VI. ZPE (in cm^{-1}) of H_5^+ and its isotopomers obtained from the MCTDH calculations using the analytical PES from Ref. 12, and their comparison with previous DMC calculations with the same surface. The position of the D atom is given according to the numbering in Fig. 1.

Species	D-position (z-grid)	This work/ MCTDH	$\Delta E_{\text{DMC-MCTDH}}$	DMC ¹³
H_5^+	-(A)	7202.6	5.4	7208 $\pm$ 4
H_4D^+	4(B)	6811.4	4.6	6816 $\pm$ 2
	5(D)	6854.1	5.9	6860 $\pm$ 1
H_3D_2^+	1,2(C)	6369.2	4.8	6374 $\pm$ 1
	1,4(D)	6421.8	-1.8	6420 $\pm$ 3
H_2D_3^+	4,5(B)	6449.9	7.1	6457 $\pm$ 1
	1,3,4(E)	5979.0	1.0	5980 $\pm$ 1
HD_4^+	3,4,5(C)	5992.0	8.0	6000 $\pm$ 4
	1,4,5(D)	6051.6	3.4	6055 $\pm$ 1
HD_4^+	1,2,3,4(A)	5535.6	-2.6	5533 $\pm$ 2
	1,2,3,5(E)	5598.5	4.5	5603 $\pm$ 7
D_5^+	1,2,3,4,5(A)	5151.0	0.0	5151 $\pm$ 1

tation of the H_5^+ and D_5^+ ZPEs, which are the upper and lower bounds of the ZPE values, respectively, of all mixed isotopic species. The potential curve along the H_3^+-H_2 distance with the H_5^+ fixed at its 1- C_{2v} orientation is also plotted, together with the well-depth, D_e , and binding energies, D_0 , for the $\text{H}_3^+ + \text{H}_2/\text{D}_3^+ + \text{D}_2$ dissociation. In Table VI, we order the isotopomers in increasing number of D atoms, and for each of them by increasing energy, that is, depending of the position of the D within the cluster. One can see that for H_4D^+ the form with the D atom in the side position is more stable than the one with it in the middle one. Again, for the H_3D_2^+ the cluster arrangements with the D atoms in the same side, and then in the opposite sides are more favorable than the one with one D atom in the central one. This is also the case for the H_2D_3^+ and HD_4^+ isotopomers, where the most stable conformers can be viewed as $\text{DH}\dots\text{D}_2\text{H}^+$ and $\text{D}_2\dots\text{D}_2\text{H}^+$, respectively, with the proton always as the central atom and the D atoms to prefer the positions within the triatomic core. The importance of

FIG. 3. Schematic diagram of the H_5^+ PES along the intermolecular distance between the centers of masses of the H_3^+ and H_2 , together with the ZPE values for the indicated $\text{H}_5^+/\text{D}_5^+$ isotopes and their corresponding $\text{H}_3^+/\text{D}_3^+$ and H_2/D_2 fragments. Well-depth, D_e , and binding energy, D_0 , values are also displayed.

FIG. 4. 3D plots of the probability density distributions of the ground vibrational state of the H_5^+ (top panel) and D_5^+ (bottom panel) together with the projection of the underlying potential surface from Ref. 12.

the ZPE of such species, formed by triatomic cations plus a diatom, has been extensively discussed in previous studies (see Ref. 13) in connection with their implication in reactive scattering, e.g., deuterium fractionation in interstellar medium.^{15–18} The present results are in completely accord with the ones previously reported by Acioli *et al.*¹³ from the DMC calculations, with differences within the statistical error of the reference DMC data in most cases, while the larger deviation of 8.0 cm^{-1} is found for the second conformer of the H_2D_3^+ (see Table VI).

In Figure 4, we present three-dimensional plots of the potential energy surface¹² together with probability density distributions of the ground vibrational state of the H_5^+ and D_5^+ , and their projections in the (R, z) -plane. The distribution functions show a peak to D_{2d} configurations, with the one corresponding to the D_5^+ to be more localized than the H_5^+ one, although both show large amplitude displacements of the central H^+/D^+ which is moving between the two symmetric C_{2v} potential wells. Figure 5 displays minimum energy paths for both potential surfaces used here^{12,23} along z and R (see left panels) and α , $\theta_{1,2}$ (see right panels) coordinates. A comparison of these PESs is described next.

Both surfaces present a double-minimum topology along z coordinate corresponding to the two symmetric $1-\text{C}_{2v}$ global minima with a relative low isomerization barrier between

them of a D_{2d} symmetry. The surface by Aguado *et al.*²³ predicts somehow higher barrier for the internal proton exchange (see left-top panel of Fig. 5) of 135 cm^{-1} compared to 52 cm^{-1} of the earlier PES,¹² while for the barrier corresponding to H_2 rotation around the C_{2v} -axis of the H_5^+ , namely, $3-\text{C}_{2v}$, the reverse ordering is obtained (see right-top panel of Fig. 5) with energies of 93 and 103 cm^{-1} , respectively. The potential curves along the R and $\theta_{1,2}$ coordinates show a similar behavior for both surfaces (see left-bottom and right-bottom panels, respectively, of Fig. 5), with the PES by Xie *et al.*¹² being more anharmonic for the intermolecular R distance between the two H_2 . The corresponding probability distributions, obtained from the PES of Ref. 23, are also depicted in Figure 5, with the ground vibrational state corresponding to the lowest one in energy. We can see that along the z coordinate a quite broad distribution is obtained, for the α coordinate the distribution is almost flat with nonzero values for the whole range of α values, while for R and θ_1 the distributions look more localized, with a clear peak at $\theta_1 = 90^\circ$. The ground state properties for the surface of Aguado *et al.*²³ are found in accord with the results of previous studies based on MCTDH, MM-RPH, DMC, and PIMC calculations using earlier reported PESs of H_5^+ ,^{12,20} and all of them predict a highly fluxional behavior with the proton shared between the two almost freely rotating H_2/D_2 diatoms. In particular, as we mentioned above (see Table III), using the PES by Aguado *et al.*²³ we obtained higher ZPEs values by 34.9, 34.6, 26.4, and 26.9 cm^{-1} for the H_5^+ , H_4D^+ , HD_4^+ , and D_5^+ , respectively, compared to those using the PES by Xie *et al.*,¹² and attributed to the differences between the two surfaces as we discussed above.

2. Vibrationally excited states

For calculating vibrationally excited states, we employed the block improved relaxation procedure⁵⁰ implemented in the Heidelberg MCTDH package.³⁵ Thus, a block of initial vectors corresponding to the number of the desired states are simultaneously computed, and then converge collectively, using the same set of SPFs for all of them, to the set of eigenstates. In Tables VII and VIII, we report the results of vibrational excited states of the H_5^+ and D_5^+ computations for both PESs.^{12,23} In the larger MCTDH calculation, we used 22, 38, 15, and 3 and 20, 38, 20, and 3 SPFs per mode for H_5^+ and D_5^+ , respectively. Converging to excited states becomes more difficult as the excitation energy increases, thus it was possible, here, to compute the first $n = 19$ lower-lying states.

The energies of these states are lying within the range up to about 1000 and 700 cm^{-1} , above the ZPEs values for the H_5^+ and D_5^+ clusters, respectively. The first 11–12 excited states correspond to excitations of the internal α rotation, or shared-proton stretching mode or combinations of them, which are the lower frequency motions of the system, and they lie at energies up to 800 and 500 cm^{-1} , for H_5^+ and D_5^+ , respectively. The next ones involve excitations of the bending $\theta_{1,2}$ modes and combinations of them, while excitations in the q_4 mode correspond to stretching of the H_2 subunits, and are expected for higher energies, around 3500 cm^{-1} . The

FIG. 5. Minimum energy path along z , R (left panel), and α , θ_1 (right panel) coordinates with H_5^+ fixed at its C_{2v} configuration. Probability distributions obtained with the PES^a for the indicated n levels are also shown, with the zero values of them shifted to their energies. PES^a from Ref. 23 and PES^b from Ref. 12.

assignments of these states are given in Tables VII and VIII for the H_5^+ and D_5^+ , respectively, while in Figures 6 and 7 we display contour plots of the probability distribution of several of them at the corresponding coordinates. One can see that, e.g., the $n = 3$ state of the H_5^+ corresponds to $v_z = 1$, with v being the quanta excitations in the indicated internal coordinate. Also, in Figure 5 we show one-dimensional probability distributions for selected states of H_5^+ using the PES by Aguado *et al.*,²³ such as $n = 1$ and 2 with 1 and 2 excitations in the α (see right-top panel), $n = 3$ with an excitation in z (see left-top panel), $n = 18$ with a node in R coordinate (see left-bottom panel) and $n = 15$ with θ_1 or θ_2 excitation (see right-bottom panel). The results reported here using the PES of Aguado *et al.*²³ are the first full-dimensional ones, and can only be compared with reduced-dimensional values reported recently.³³ In particular, from a 7D calculation ZPE of 7167.1 cm^{-1} has been obtained for the H_5^+ , which is by 70 cm^{-1} lower due to the contribution of the 2 more degrees of freedom. Five excited vibrational states have been also computed, although as H_5^+ is highly coupled system the differences are rather large, for example, the $n = 3$ state, corresponding to the shared-proton stretch-mode, is predicted at energy of

353.5 cm^{-1} from the present full MCTDH calculations, while the 7D value for this state was 255.5 cm^{-1} .³³

However, in Table VII, we compare the present results with the ones available from previous studies employing the surface by Xie *et al.*,¹² from MCTDH, MM-RPH, DMC, and PIMC calculations.^{5,13,28,29} We should point out that the four-mode combination scheme employed here differs from five-mode one used previously in the MCTDH study of the H_5^+ ,²⁹ in which the R_1 and R_2 coordinates were not grouped together. By comparing now the results obtained using the two different schemes, we can see small differences in the energies of the states that, in principal, should be attributed to the n -mode representation of the PES, and are within the convergence error in the MCTDH calculations of about 10 cm^{-1} for the H_5^+ at the whole range of energies studied.

Further, in Tables VII and VIII, we compare with data reported previously by DMC, MM-RPH, and PIMC approaches on the ground, and an other two vibrational excited states, corresponding to the shared-proton stretching and torsional modes, using the same underlying surface,^{5,13,28} for the H_5^+ and D_5^+ , respectively. The present MCTDH energies for these states are 92.6 and 365.4 cm^{-1} for the H_5^+ and 36.9 and

TABLE VII. ZPE values (in cm^{-1} , energy is relative to the potential minimum) and vibrational energies (in cm^{-1} , energies are relative to the corresponding ZPE value) for the n indicated states of H_3^+ together with their assignment obtained from the MCTDH calculations. Comparison with previous MCTDH,²⁹ MM-RPH,⁵ DMC,^{5,13} and PIMC²⁸ data is also presented. PES^a from Ref. 23 and PES^b from Ref. 12.

MCTDH (this work)			MCTDH ²⁹	MM-RPH ⁵	DMC ^{5,13}	PIMC ²⁸
PES ^a /PES ^b			PES ^b			
	Energy	State				
<i>n</i>	7237.5/7202.6	ZPE	7210.3	7244	7208 ± 4/7210	7154 ± 88
1	90.9/92.6	<i>v</i> _α =1 (even)	96.3	66	80	...
2	136.2/133.3	<i>v</i> _α =1 (odd)	135.7	...	...	...
3	353.5/365.4	<i>v</i> _z =1	358.7	382	334	...
4	449.4/447.1	<i>v</i> _α =2 (even)	452.9	...	...	...
5	452.1/452.3	<i>v</i> _α =2 (odd)	453.6	...	...	...
6	449.7/462.8	<i>v</i> _z , <i>v</i> _α =1 (even)	464.4	...	...	...
7	486.7/495.9	<i>v</i> _z , <i>v</i> _α =1 (odd)	495.1	...	...	...
8	695.7/679.5	<i>v</i> _z , <i>v</i> _R =1	673.6	...	...	...
9	792.2/779.5	<i>v</i> _z , <i>v</i> _R , <i>v</i> _α =1 (even)	784.3	...	...	...
10	830.0/808.2	<i>v</i> _z , <i>v</i> _R , <i>v</i> _α =1 (odd)	809.4	...	...	...
11	814.7/819.8	<i>v</i> _z =1, <i>v</i> _α =2 (even)	822.0	...	...	...
12	818.3/826.9	<i>v</i> _z =1, <i>v</i> _α =2 (odd)	825.3	...	...	...
13	835.9/831.1	<i>v</i> _{θ₁−θ₂} (α = 0)	825.4	...	...	...
14	834.5/834.7	<i>v</i> _{θ₁+θ₂} (α = π)	846.0	...	...	...
15	919.3/920.2	<i>v</i> _{θ₂} , <i>v</i> _α =1 (even)	930.3	...	...	...
16	921.2/922.1	<i>v</i> _{θ₁} , <i>v</i> _α =1 (even)	940.1	...	...	...
17	1032.8/1012.6	<i>v</i> _{θ₁−θ₂} (α = 0)/ <i>v</i> _α =3 (even)	1017.2	...	...	...
18	1072.8/1019.1	<i>v</i> _z = <i>v</i> _R =1/ <i>v</i> _α =3 (odd)	1025.9	...	...	...
19	1032.4/1029.1	<i>v</i> _{θ₁+θ₂} (α = 0)	1029.4	...	...	...

TABLE VIII. Same as Table VII for the ZPE values (in cm^{-1}) and vibrational energies (in cm^{-1} , energies are relative to the corresponding ZPE value) for the n indicated states of D_3^+ .

	MCTDH (this work)		MM-RPH ⁵	DMC ^{5,13}	PIMC ²⁸
	PES ^a /PES ^b			PES ^b	
<i>n</i>	Energy	State			
	5177.9/5151.0	ZPE	5174	5151 ± 1	5082 ± 77
1	35.9/36.9	<i>v</i> _α =1 (even)	28	32	...
2	82.3/81.5	<i>v</i> _α =1 (odd)	...	...	...
3	227.0/225.0	<i>v</i> _α =2 (even)	...	...	...
4	229.4/231.6	<i>v</i> _α =2 (odd)	...	...	...
5	225.0/238.1	<i>v</i> _z =1	257	222	...
6	263.5/278.2	<i>v</i> _z , <i>v</i> _α =1 (even)	...	...	...
7	303.0/316.6	<i>v</i> _z , <i>v</i> _α =1 (odd)	...	...	...
8	463.1/458.5	<i>v</i> _z , <i>v</i> _R =1	...	...	...
9	452.3/463.9	<i>v</i> _z =1, <i>v</i> _α =2 (even)	...	...	...
10	452.7/472.2	<i>v</i> _z =1, <i>v</i> _α =2 (odd)	...	...	...
11	502.7/501.8	<i>v</i> _z , <i>v</i> _R , <i>v</i> _α =1 (even)	...	...	...
12	630.4/508.9	<i>v</i> _{θ₁−θ₂} , <i>v</i> _α =1 (even)/ <i>v</i> _α =3 (even)	...	...	...
13	687.6/511.0	<i>v</i> _z = <i>v</i> _R =1/ <i>v</i> _α =3 (odd)	...	...	...
14	540.9/534.8	<i>v</i> _z , <i>v</i> _R , <i>v</i> _α =1 (odd)	...	...	...
15	586.4/592.0	<i>v</i> _{θ₁−θ₂} (α = 0)	...	...	...
16	586.1/592.2	<i>v</i> _{θ₁+θ₂} (α = π)	...	...	...
17	627.7/632.1	<i>v</i> _{θ₂} , <i>v</i> _α =1 (even)	...	...	...
18	692.7/632.2	<i>v</i> _z , <i>v</i> _R =1, <i>v</i> _α =2 (odd)/ <i>v</i> _{θ₁} , <i>v</i> _α =1 (even)	...	...	...
19	693.7/683.5	<i>v</i> _z , <i>v</i> _R =1, <i>v</i> _α =2 (even)	...	...	...

FIG. 6. 2D contour plots of the probability density distributions for the ground and the indicated excited vibrational states of the H_5^+ using the potential surface of Ref. 23.

238.1 cm^{-1} for the D_5^+ , which are compared very well with the results from the fixed-node DMC calculations of 80 and 334 cm^{-1} and 32 and 222 cm^{-1} for H_5^+ and D_5^+ , respectively. Somehow larger differences are found comparing them with the MM-RPH values, with the MCTDH energies being higher

for the shared-proton stretch and between the DMC and MM-RPH results for the torsional mode for both isotopomers.

As we discussed above, the two analytical PESs^{12,23} show small differences (see Fig. 5 at the energy range of interest, and by comparing the results on the vibrational states

FIG. 7. 2D contour plots of the probability density distributions for the ground and the indicated excited vibrational states of the D_5^+ cluster using the PES^a (left-size panels) and PES^b (right-size panels) from Refs. 12 and 23, respectively.

of the H_5^+ and D_5^+ we found different ordering of the states, e.g., $n = 5$ and 6 or $n = 10$ and 11 for H_5^+ , and $n = 3$ and 5 or $n = 8, 9$, and 10 for the D_5^+ . Given that the convergence achieved in the MCTDH calculations for both surfaces is almost the same, we may conclude that both of them predict very similar behavior of the vibrational state of the H_5^+ systems. As seen the differences between them are mainly reflected in the energies of the shared-proton and its combinations modes, especially for the D_5^+ , where the convergence in the MCTDH calculations is better than in the H_5^+ ones.

III. SUMMARY AND CONCLUSIONS

We carried out a theoretical investigation on the vibrational levels of H_5^+ and its deuterated counterparts. These cations are highly floppy and any sort of analysis based on standard zeroth-order models is not expected to be useful. The 120 equivalent global minima are separated by very low po-

tential barriers and even the vibrational ground state is highly delocalized over the lowest stationary points of the surface.

In this work, we take advantage of recent computational/methodological progress made on the generation of PESs, here for H_5^+ , and the availability of performing a full-dimensional quantum treatment within the MCTDH framework. Two different, recent analytical PESs are employed in the present computations. For the 9D MCTDH calculations each PES is approximated by a n -mode representation introducing an adequate four-mode combination scheme to obtain a computationally compact and manageable representation. An analysis of the accuracy of the n -mode expansion up to third-order terms is performed. The ZPE for each isotope is computed by improved relaxation calculations and an excellent agreement, within few cm^{-1} , with the reference DMC results, is found for all cases. The ZPE decreases as the number of deuterium atoms increases, with the D atoms to prefer the external positions in the cluster, and maximizing their number in the H_3^+ core. The differences between the ZPE of these

isotopologues are indicative, and of particular interest for the study of interstellar chemistry reaction mechanisms, i.e., deuterium fractionation.

Further, the first 20 vibrational excited states, that are related to the internal H_2 rotation, shared-proton stretching, symmetric, and antisymmetric bending motions and combinations of them, are calculated from block-improved relaxation computations for both H_5^+ and D_5^+ isotopomers. The computed energies for the torsion splitting and excitation of the shared-proton mode are compared very well with the ones available from fixed-node DMC calculations. The energies of the vibrational states present important shifts to lower frequencies upon deuterium substitution.

The reported results provide important information on the spectroscopy of H_5^+/D_5^+ complexes in a rigorous manner, and open perspectives for a full-dimensional simulation, using the MCTDH approach, of the IR photodissociation spectra recorded recently for both H_5^+ and D_5^+ clusters. As we discussed both analytical surfaces employed show small differences at the energy range studied, predicting very similar energy level patterns for the H_5^+ and D_5^+ isotopomers. Unfortunately, no experimental results are yet available at the low energy regime, to allow us for a further evaluation of them.

However, apart for a reliable representation scheme for the H_5^+ PES, a dipole moment surface is also required, and further several technical modifications should be considered to reach the higher energy regime of the vibrationally predissociating states with R_1/R_2 excitations, where experimental measurements are available. Work in this direction is in progress.

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APPENDIX: KINETIC ENERGY OPERATOR

Following the framework described in Refs. 39–41, the KEO in the $(R, R_1, R_2, x, y, z, \theta_1, \theta_2, \alpha)$ coordinates for zero total angular momentum, reads⁴²

$$\begin{aligned} \hat{T} = & -\frac{\hbar^2}{2\mu_R}\partial_R^2 - \frac{\hbar^2}{2\mu_1}\partial_{R_1}^2 - \frac{\hbar^2}{2\mu_2}\partial_{R_2}^2 - \frac{\hbar^2}{2m}(\partial_x^2 + \partial_y^2 + \partial_z^2) - \hbar^2 \left(\partial_{u_{\theta_1}}(1 - u_{\theta_1}^2)\partial_{u_{\theta_1}} \right. \\ & + \frac{1}{1 - u_{\theta_1}^2}(\partial_\alpha^2 + x^2\partial_y^2 + y^2\partial_x^2 - x\partial_x\partial_y y - y\partial_y\partial_x x + 2x\partial_y\partial_\alpha - 2y\partial_x\partial_\alpha) \left. \left(\frac{1}{2\mu_R R^2} + \frac{1}{2\mu_1 R_1^2} \right) \right. \\ & - \hbar^2 \left(\partial_{u_{\theta_2}}(1 - u_{\theta_2}^2)\partial_{u_{\theta_2}} + \frac{1}{1 - u_{\theta_2}^2}\partial_\alpha^2 \right) \left(\frac{1}{2\mu_R R^2} + \frac{1}{2\mu_2 R_2^2} \right) \\ & - \frac{\hbar^2}{2\mu_R R^2} \left[-2\partial_\alpha \cos \alpha \frac{u_{\theta_1}}{\sin \theta_1} \frac{u_{\theta_2}}{\sin \theta_2} \partial_\alpha - (x\partial_y - y\partial_x) \cos \alpha \frac{u_{\theta_1}}{\sin \theta_1} \frac{u_{\theta_2}}{\sin \theta_2} \partial_\alpha \right. \\ & - \partial_\alpha \cos \alpha \frac{u_{\theta_1}}{\sin \theta_1} \frac{u_{\theta_2}}{\sin \theta_2} (x\partial_y - y\partial_x) + \partial_\alpha \sin \alpha \frac{u_{\theta_1}}{\sin \theta_1} \sin \theta_2 \partial_{u_{\theta_2}} + \partial_{u_{\theta_2}} \sin \alpha \frac{u_{\theta_1}}{\sin \theta_1} \sin \theta_2 \partial_\alpha \\ & + (x\partial_y - y\partial_x) \sin \alpha \frac{u_{\theta_1}}{\sin \theta_1} \sin \theta_2 \partial_{u_{\theta_2}} + \partial_{u_{\theta_2}} \sin \alpha \frac{u_{\theta_1}}{\sin \theta_1} \sin \theta_2 (x\partial_y - y\partial_x) \\ & + \partial_{u_{\theta_1}} \sin \alpha \sin \theta_1 \frac{u_{\theta_2}}{\sin \theta_2} \partial_\alpha + \partial_\alpha \sin \alpha \sin \theta_1 \frac{u_{\theta_2}}{\sin \theta_2} \partial_{u_{\theta_1}} + \partial_{u_{\theta_1}} \cos \alpha \sin \theta_1 \sin \theta_2 \partial_{u_{\theta_2}} \\ & \left. + \partial_{u_{\theta_2}} \cos \alpha \sin \theta_1 \sin \theta_2 \partial_{u_{\theta_1}} - 2\partial_\alpha^2 - 2\partial_\alpha (x\partial_y - y\partial_x) \right] \\ & - \frac{\hbar^2}{2\mu_R R^2} (y^2\partial_z^2 + z^2\partial_y^2 + z^2\partial_x^2 + x^2\partial_z^2 - x^2\partial_y^2 - y^2\partial_x^2 \\ & - y\partial_y\partial_z z - \partial_y y z \partial_z - \partial_x x z \partial_z - x\partial_x\partial_z z + x\partial_x\partial_y y + \partial_x x y \partial_y) \\ & + \frac{\hbar^2}{2\mu_R R^2} \left[\left(-2\frac{u_{\theta_1}}{\sin \theta_1} \partial_\alpha + \frac{u_{\theta_2}}{\sin \theta_2} \cos \alpha \partial_\alpha + \partial_\alpha \frac{u_{\theta_2}}{\sin \theta_2} \cos \alpha - \sin \alpha \sin \theta_2 \partial_{u_{\theta_2}} \right. \right. \\ & \left. \left. - \partial_{u_{\theta_2}} \sin \alpha \sin \theta_2 \right) (y\partial_z - z\partial_y) + \left(\sin \theta_1 \partial_{u_{\theta_1}} + \partial_{u_{\theta_1}} \sin \theta_1 + \sin \alpha \frac{u_{\theta_2}}{\sin \theta_2} \partial_\alpha \right. \right. \end{aligned}$$

$$\begin{aligned}
& + \partial_\alpha \sin \alpha \frac{u_{\theta_2}}{\sin \theta_2} + \cos \alpha \sin \theta_2 \partial_{u_{\theta_2}} + \partial_{u_{\theta_2}} \cos \alpha \sin \theta_2 \Big) (z \partial_x - x \partial_z) \Big] \\
& - \frac{\hbar^2}{2\mu_R R^2} \left[\frac{u_{\theta_1}}{\sin \theta_1} (x \partial_y y \partial_z + x y \partial_y \partial_z - 2x \partial_y^2 z - 2\partial_x y^2 \partial_z + \partial_x y \partial_y z + \partial_x \partial_y y z) \right], \quad (\text{A1})
\end{aligned}$$

where $u_{\theta_{1,2}} = \cos \theta_{1,2}$, and the reduced masses are defined in Eq. (1).

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