

MARVEL analysis of the rotational–vibrational states of the molecular ions H_2D^+ and D_2H^+ †

Cite this: *Phys. Chem. Chem. Phys.*, 2013, **15**, 10181

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Critically evaluated rotational–vibrational line positions and energy levels, with associated critically reviewed labels and uncertainties, are reported for two deuterated isotopologues of the H_3^+ molecular ion: H_2D^+ and D_2H^+ . The procedure MARVEL, standing for Measured Active Rotational–Vibrational Energy Levels, is used to determine the validated levels and lines and their self-consistent uncertainties based on the experimentally available information. The spectral ranges covered for the isotopologues H_2D^+ and D_2H^+ are 5.2–7105.5 and 23.0–6581.1 cm^{-1} , respectively. The MARVEL energy levels of the *ortho* and *para* forms of the ions are checked against ones determined from accurate variational nuclear motion computations employing the best available adiabatic *ab initio* potential energy surfaces of these isotopologues. The number of critically evaluated, validated and recommended experimental (levels, lines) are (109, 185) and (104, 136) for H_2D^+ and D_2H^+ , respectively. The lists of assigned MARVEL lines and levels and variational levels obtained for H_2D^+ and D_2H^+ as part of this study are deposited in the ESI to this paper.

Received 20th December 2012,

Accepted 17th April 2013

DOI: 10.1039/c3cp44610g

www.rsc.org/pccp

1 Introduction

The isotopologues of the H_3^+ molecular ion contain three nuclei and two electrons; thus, they form the simplest class of polyatomic molecules of considerable practical importance.^{1–4} These highly stable ions are easily formed *via* variants of the strongly exothermic reaction $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ and drive the chemistry in many cold parts of the universe, where only barrierless reactions, including the ion–molecule reactions $\text{H}_3^+ + \text{X} \rightarrow \text{HX}^+ + \text{H}_2$ and their variants (X can be an atom or a molecule), are feasible.^{5,6} Isotopologues of the H_3^+ ions are important tracers of the chemistry of the colder (less than 20 K) and warmer (30–100 K) parts of the interstellar medium (ISM).^{7–9} Under about 10 K, the deuterated forms of the H_3^+ ion become dominant in molecular clouds (of the two isotopologues H_2D^+ is usually the more abundant due to the slight exothermicity of the D exchange reactions though under extreme circumstances, when all the molecules, like CO_2 , are frozen out onto grains, H_2D^+ and D_2H^+ are predicted to have equal abundances), allowing straightforward detection of the ions *via* far-infrared and submillimeterwave spectroscopies in the ISM.

The electronic structure of the H_3^+ isotopologues is simple, the ground electronic state is relatively well separated from all

the excited electronic states,^{10–16} although avoided crossings do arise between the ground state and the first two excited singlet states when a global potential energy surface (PES) is considered. Thus, to understand the complete spectroscopy of the electronic ground state detailed knowledge of several excited states is necessary.¹⁵ The equilibrium structure of the ground electronic states of H_3^+ and D_3^+ is an equilateral triangle, corresponding to D_{3h} point-group symmetry (the Born–Oppenheimer equilibrium structures of H_2D^+ and D_2H^+ also belong to this point-group symmetry). Being nonlinear triatomic molecules, these ions have only three vibrational degrees of freedom. For H_2D^+ and D_2H^+ , the degenerate bending mode ν_2 of H_3^+ is split into a bending and an asymmetric stretching mode, ν_2 and ν_3 , respectively (as determined in this study, the splitting is 129.549(5) and 110.27(1) cm^{-1} for H_2D^+ and D_2H^+ , respectively, with the bending fundamental being lower in energy). Unlike their symmetric top parent, the H_2D^+ and D_2H^+ isotopologues are asymmetric tops; in fact, H_2D^+ is one of the most perfect asymmetric tops with a κ (Ray-asymmetry)^{17,18} parameter value of -0.07 .

The nuclear dynamics of these benchmark ions³ exhibits several unusual features. Due to the lightness of all the atoms of the ions, their vibrations are of very large amplitude, separation of the vibrational and rotational degrees of freedom is poor, and adiabatic and nonadiabatic effects become overly important when one tries to reproduce or predict the ions' high-resolution spectra.¹⁹ The usual perturbational treatments and effective Hamiltonians used for interpreting molecular spectra have poor convergence characteristics for these very

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3cp44610g

light ions.²⁰ Thus, only variational techniques are applicable for the interpretation of the complex rotational–vibrational spectra of the ions, which are also rather hard to observe due to the low absorption intensities. Sophisticated variational nuclear motion techniques, whose results are limited in accuracy principally by the accuracy of the PES employed and the nonadiabatic effect, have been developed to treat some or all of the bound rovibrational states and also resonance states beyond the first dissociation asymptote.^{21–32}

Initiated by work of Shy *et al.*³³ and the Oka group,^{34,35} high-resolution spectra of the H_3^+ isotopologues have been the subject of a number of experimental investigations, resulting in a considerable quantity of data for H_2D^+ (ref. 19, 36–50) and D_2H^+ .^{20,43–45,48,49,51–54} A huge number of measured transitions exist in near-dissociation spectra^{55,56} but these have not been assigned; thus, they cannot form part of the present study. The last comprehensive, critical evaluation of the measured data for H_3^+ was performed in 2001 by Lindsay and McCall.⁵⁷ An update of this work is underway in our laboratory and its results will be reported in the future. To the best of our knowledge no comprehensive, critical evaluation of the measured data is available for H_2D^+ and D_2H^+ , apart from the attempt of Kozin *et al.*⁴³ A number of theoretical studies^{23,58,59} investigated the rovibrational energy levels and transitions of H_2D^+ and D_2H^+ . There is a recent comprehensive, high-accuracy linelist available for H_2D^+ containing over 22 million transitions among more than 33 000 rovibrational energy levels (all levels below $18\,500\text{ cm}^{-1}$ with rotational quantum number $J \leq 20$).⁵⁹ No similar extensive linelist is available for D_2H^+ .

In the present study, we perform a systematic analysis of the rovibrational spectra corresponding to the ground electronic states of H_2D^+ and D_2H^+ , utilizing the MARVEL protocol and code,^{60–62} where MARVEL stands for Measured Active Rotational–Vibrational Energy Levels. MARVEL can invert, in a weighted least-squares sense, the measured transition data and results in accurate, experimental-quality energy levels with dependable uncertainties (if the measurement uncertainties are accurate). The method has been employed successfully to determine the rovibrational states of several water isotopologues^{63–65} and of parent ketene.⁶⁶

There are several reasons why it is convenient to convert transition wavenumbers to energy levels and why it offers new physical insight. First, this process reduces the volume of experimental information considerably, for molecules thoroughly studied spectroscopically^{63–65,67,68} by orders of magnitude (determination of spectroscopic parameters offers even larger savings but this approach is not considered here for several reasons, including that its predictive power is rather limited). Second, once a set of experimentally derived energy levels is available, not only the wavenumbers of the line centers can be restored with practically experimental accuracy but they also allow to make new assignments in existing spectra or provide an improved basis for assignments of new spectra. Third, it is more natural to compare (variationally) computed and experimentally derived energy levels and not transitions. Fourth, a MARVEL-type procedure can help, as demonstrated before,⁶⁹ to reduce the uncertainty with which a transition has been determined. Fifth, accurate energy-level lists,

such as those presented here for two H_3^+ isotopologues, provide an excellent starting point for the computation of ideal-gas partition functions and related thermodynamic and thermochemical properties.⁷⁰ Sixth, determination of the best labeled energy levels and transitions helps to understand the true nature of the spectroscopic network (SN)^{67,68} of a molecule. These arguments explain partly why the present study was undertaken.

A distinguishing feature of the present study is the joint utilization of all available experimental and the best theoretical transition and energy level data. While determination of complete linelists is outside the scope of present-day experiments, they can be determined by means of sophisticated first-principles computations. Consequently, as long as experiments have a higher accuracy than even the most advanced computations that can be performed for the H_3^+ isotopologues, the complete linelist will necessarily contain accurate experimental data and less accurate computed data (the same holds for all other molecules, as well). MARVEL-type efforts help to replace as many computed levels and lines as possible with their experimental counterparts paving the way to an understanding of the complete spectra of the H_3^+ isotopologues.

2 The MARVEL methodology

The methods employed in this study for collecting and critically evaluating experimental transition wavenumbers and uncertainties and for inverting the wavenumbers in order to obtain the best possible energy levels with attached uncertainties are based on the MARVEL procedure developed by Furtenbacher and Császár.^{60–62} MARVEL simultaneously processes all the available assigned experimental lines and determines the associated energy levels for the chosen isotopologue. While the energy levels obtained could be called empirical, in order to emphasize the process they were derived from, the evaluated and validated energy levels will be called MARVEL energy levels.

In the present work the steps detailed below were followed to go from measured and assigned experimental transitions to MARVEL energy levels.

First, all experimental high-resolution spectroscopic data known to us were gathered for both isotopologues. Only published, directly measured transition data were considered. Tables 1 and 2 list the experimental sources of transition data collected during the course of the present study for H_2D^+ and D_2H^+ , respectively. The number of originally measured and assigned (A) and validated (V) transitions for each data source, represented by a suitably chosen tag, is given in these tables. The lines and levels are given in the ESI† to this paper.⁷¹ In order to be used in MARVEL, each transition has to have an initial nonzero uncertainty representing as closely as possible the true accuracy of the measured line. In most cases these uncertainties can be taken directly from the source but in several cases they had to be guessed from the papers describing the measurements. Note that if a transition is not connected to one of the principal components of the spectroscopic network of either H_2D^+ or D_2H^+ (see Section 3 for more details about SNs), this transition cannot be validated within the MARVEL protocol.

Table 1 Data sources of experimental line information for the H₂D⁺ ion

Tag	Range/cm ⁻¹	Trans.(A/V) ^a	Comments ^b
85SaKaHi ⁴¹	5.2	1/1	1c
05AmHi ⁴⁵	5.2–45.7	4/3	1d
09YoMaMoTa ⁵⁰	5.2–115.2	8/8	1e
84BoDeDeDe ³⁸	12.4	1/1	1f
84WaCoPeWo ³⁹	12.4	1/1	1g
06Amano ⁴⁶	45.7–115.2	4/4	1h
08AsRiMuWi ⁴⁹	45.7	1/1	1i
86FoMcPeWa ⁴²	1837.5–2602.1	73/66	1j
84AmWa ³⁷	2839.0–3178.9	27/25	1k
85Amano ⁴⁰	2839.3–3208.1	37/37	1l
07AsHuMuKu ⁴⁸	2946.8–7105.5	27/27	1m
02FaDaKoPo ⁴⁴	4271.0–4538.4	8/8	1n
06HlKoPlKo ⁴⁷	6459.0–6491.3	3/3	1o

^a Trans. = number of transitions, A = assigned in the original source, V = validated during the present study. ^b Comments can be found in the ESI to this paper.^{7†}

Table 2 Data sources of experimental line information for the D₂H⁺ ion

Tag	Range/cm ⁻¹	Trans.(A/V) ^a	Comments ^b
03HiAm ⁵³	23.0	1/1	2c
05AmHi ⁴⁵	23.0–49.2	3/3	2d
08AsRiMuWi ⁴⁹	49.2	1/1	2e
86FoMcWa ²⁰	1782.2–2290.8	88/75	2f
90PoMc ⁵²	2275.8	1/1	2g
84LuAm ⁵¹	2637.5–2990.1	34/29	2h
02FaDaKoPo ⁴⁴	3846.7–4121.7	16/16	2i
07AsHuMuKu ⁴⁸	6466.9–6581.1	7/7	2j
06HlPlBaKo ⁵⁴	6534.3–6536.3	3/3	2k

^a Trans. = number of transitions, A = assigned in the original source, V = validated during the present study. ^b Comments can be found in the ESI to this paper.^{7†}

Thus, these transitions and their labels could be perfectly valid but are not considered to be validated by the present study.

The second step involves cleaning the data. Several tests have been performed to check the labels of the assigned transitions. Conflicts arising from the transcription of data were also identified and corrected.

The third step involves the actual execution of the MARVEL process. At this stage the uncertainties of the lines measured are adjusted *via* robust reweighting⁷² until a consistent set of experimental uncertainties are obtained. Uncertainties of energy levels reported in this paper are given by eqn (5) of ref. 61 and correspond to 95% confidence limits which are therefore 2σ.

Wavenumber calibration in certain experiments can be an issue, as this has the potential of leading to systematic shifts in the reported transitions. Unlike in some recent MARVEL-based studies,^{63–65} utilizing a much larger set of high-quality experimental data coming from Fourier-transform spectroscopy, no recalibration was attempted during the course of this work.

3 Components of SNs of the H₂D⁺ and D₂H⁺ isotopologues

The transitions collected for the two isotopologues considered in this study form spectroscopic networks (SN),^{67,68} which are large,

finite, weighted, and rooted graphs, where the vertices are discrete energy levels (with associated uncertainties), the edges are transitions (with their associated measured uncertainties), and the weights of the edges, if introduced, are provided by transition intensities characteristic of the measurement technique. Components of SNs contain all interconnecting rotational–vibrational energy levels supported by the grand database of the transitions. This, for example, means that transitions involving “*ortho*” or “*para*” spin isomers form separate components of SNs. Fig. 2 and 3 depict components of the SNs of H₂D⁺ and D₂H⁺, showing their overall structure. As suggested by these figures and depicted in Fig. 5 for both H₂D⁺ and D₂H⁺, the measured transitions exhibit a scale-free behavior, similarly to what was observed before for much larger experimental datasets.^{67,68} The somewhat uneven structure of the degree distribution curves of Fig. 5 is due to the relatively small number of measured transitions for the two ions. For spectroscopic applications it is important to note that scale-free networks are characterized by relatively few highly connected nodes (hubs) which form the set of best determined energy levels after a MARVEL analysis.

MARVEL results in the correct absolute energy levels for components not containing the global root of the SN only if the value of their lowest-energy level, zero by definition, is shifted to the correct transition energy. Since, due to the appropriate selection rules, *ortho-para* transitions cannot be measured directly (otherwise the two components would not be distinct), the difference must be estimated based on empirical and/or theoretical considerations. Due to the availability of approximate rotational Hamiltonians, which are accurate for the lowest levels, this usually presents no hindrance in the determination of highly accurate absolute energy levels for the spin isomer components. Unfortunately, for H₂D⁺ and D₂H⁺ there is only a very limited number of pure rotational transitions measured (see Tables 1 and 2). This also explains the presence of floating components (FC), *i.e.*, vertices not connected to any of the roots of the principal components (PC), as seen on Fig. 1–4. Some of the previous studies of the spectroscopy of H₂D⁺ and D₂H⁺ remedied this problem by appending the list of measured transitions with so-called combination difference (CD) “transitions”. This otherwise useful approach was not followed during the present study, strictly only measured transitions were included in the MARVEL input. When comparing the MARVEL energy levels with their variationally computed counterparts it became clear that several of the “CD transitions” introduced in the analysis were considerably less accurate than the average accuracy of the measurements.

In addition to selection rules based on “rigorous” quantum numbers, there are several approximately good quantum numbers which help to understand and characterize nuclear motion states and thus SNs. These are especially useful at low(er) energies since at higher energies they lose their physical meaning, though still can be used in defining “approximate” selection rules. In the case of the vibrations of the asymmetric top isotopologues H₂D⁺ and D₂H⁺, a useful choice for the labeling of the levels is provided by the usual standard normal mode quantum numbers (ν₁ν₂ν₃). In this notation ν₁, ν₂, and ν₃ stand for the symmetric stretching, bending, and antisymmetric

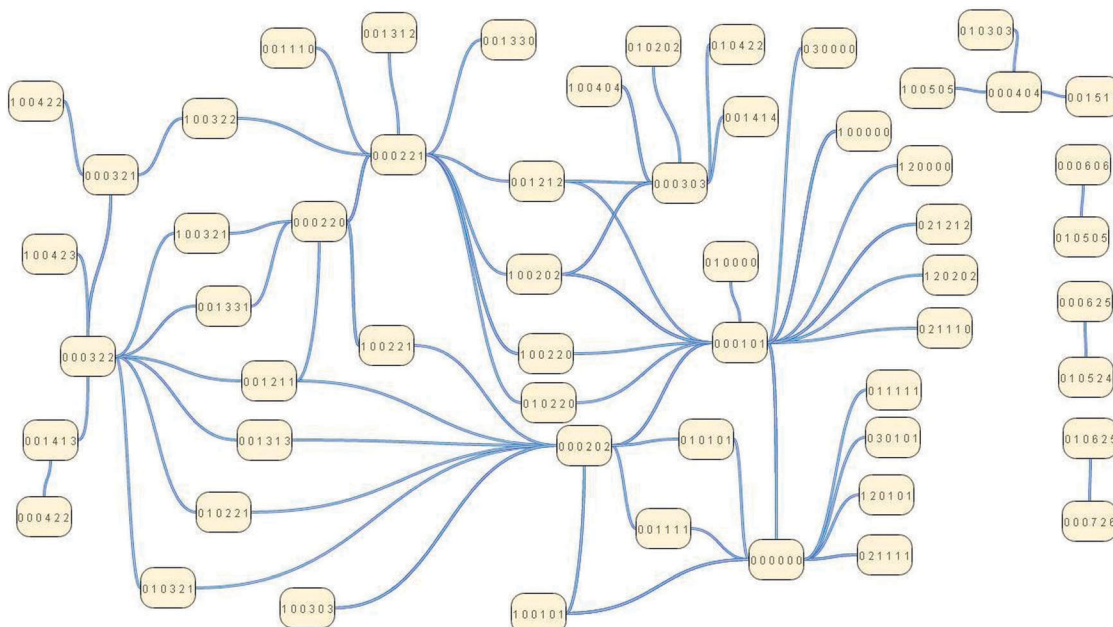


Fig. 1 Components of the measured spectroscopic network (SN) corresponding to *para*-H₂D⁺; the root is the (0 0 0) 0₀₀ level (denoted here as (0 0 0 0 0 0)), a hub within the SN.

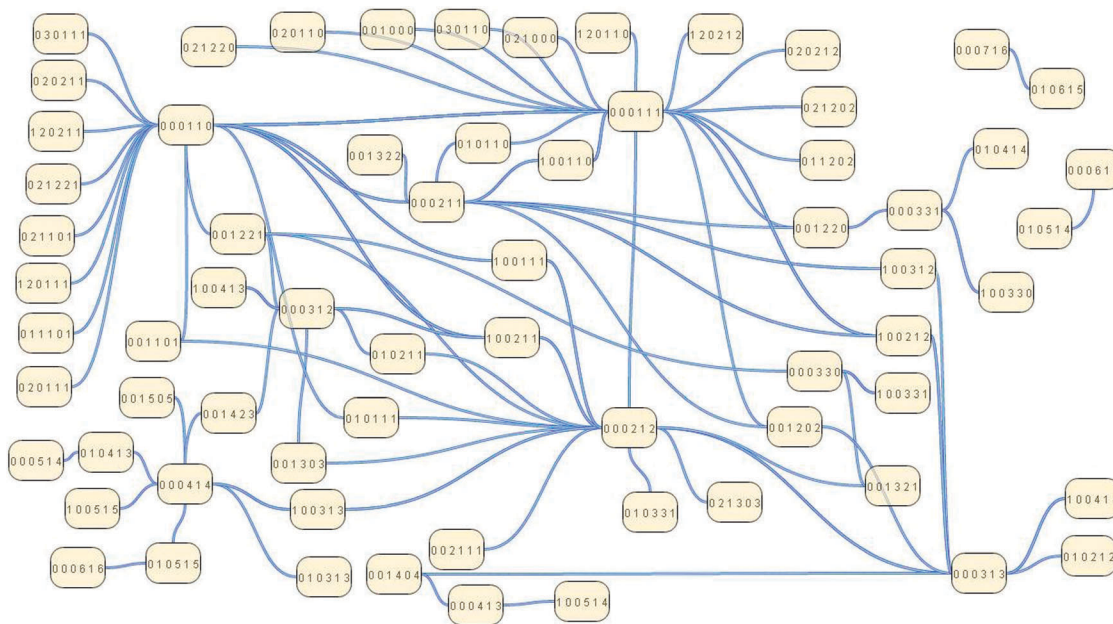


Fig. 2 Components of the measured spectroscopic network (SN) corresponding to *ortho*-H₂D⁺; the root is the (0 0 0) 1₁₁ level (denoted here as (0 0 0 1 1 1)), a hub within the SN.

stretching quantum numbers, respectively. We use the standard asymmetric top quantum numbers $J_{K_a K_c}$ to label the rotationally excited states of these isotopologues.⁷³ Thus, the rotation–vibration levels of these two deuterated isotopologues of H₃⁺ are identified uniquely by labels containing six integers altogether.

Both H₂D⁺ and D₂H⁺ belong to the C_{2v}(M) molecular symmetry (MS) group.⁷³ For H₂D⁺ and D₂H⁺ the *a* and *b* principal axes are along the C₂ axis, respectively. For H₂D⁺, the allowed symmetries of the complete internal motion wavefunction correspond to

$\Gamma^+ = B_2$ and $\Gamma^- = B_1$, while for D₂H⁺ they are $\Gamma^+ = A_1$ and $\Gamma^- = A_2$, where Γ^+ and Γ^- refer to those irreducible representations of the MS group for which the Pauli principle is satisfied with even or odd parities, respectively. For H₂D⁺, the 12 possible nuclear spin states span the representation $\Gamma_{\text{ns}}^{\text{tot}} = 9A_1 \oplus 3B_2$ (ns = nuclear spin), providing spin-statistical weights for the rovibronic states with different rovibronic Γ_{rve} symmetry labels. As the $\Gamma_{\text{rve}} \otimes \Gamma_{\text{ns}} \supset \Gamma^+$ or $\Gamma_{\text{rve}} \otimes \Gamma_{\text{ns}} \supset \Gamma^-$ relations must hold, the allowed rovibronic symmetries (in fact rotational–vibrational,

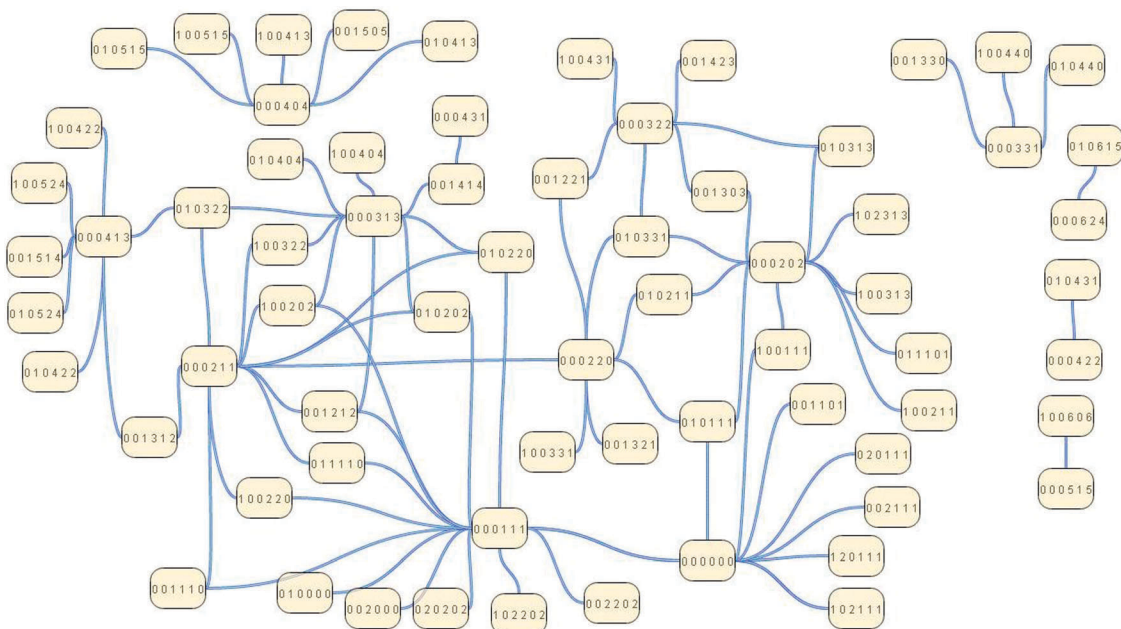


Fig. 3 Components of the measured spectroscopic network (SN) corresponding to *ortho*-D₂H⁺; the root is the (0 0 0) _{0₀₀} level (denoted here as (0 0 0 0 0 0)), a hub within the SN.

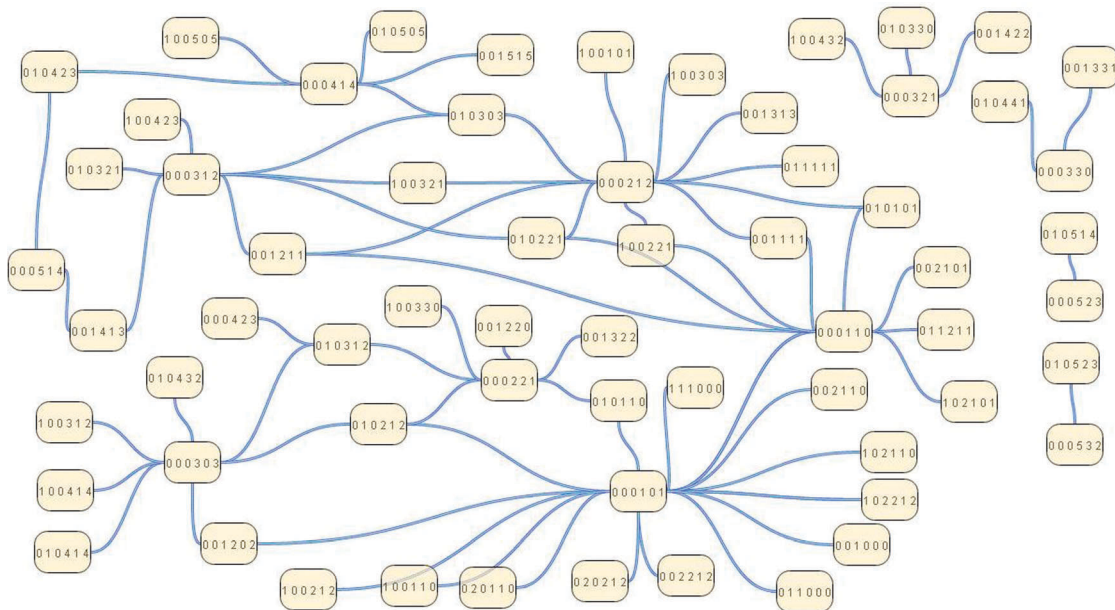


Fig. 4 Components of the measured spectroscopic network (SN) corresponding to *para*-D₂H⁺; the root is the (0 0 0) _{1₀₁} level (denoted here as (0 0 0 1 0 1)), a hub within the SN.

since we are dealing with a singlet (ground) electronic state) are B_1 and B_2 (with a spin-statistical weight of 9) for $\Gamma_{ns} = A_1$, while A_1 and A_2 (with a spin-statistical weight of 3) for $\Gamma_{ns} = B_2$. For D₂H⁺, $\Gamma_{ns}^{\text{tot}} = 12A_1 \oplus 6B_2$. Therefore, the allowed rovibronic symmetries are A_1 and A_2 (with a spin-statistical weight of 12) for $\Gamma_{ns} = A_1$, while B_1 and B_2 (with a spin-statistical weight of 6) for $\Gamma_{ns} = B_2$. The symmetry characteristics listed are collected into Table 3.

Next, we list selection rules related to approximate quantum numbers. They are based on symmetry relations presented in

Table 3 and on the rule that transitions can occur only between (a) levels of the same rooted components of the SN due to the orthogonality of the nuclear spin states, and (b) levels with different parities as the parity of the dipole moment operator is odd. For H₂D⁺, the *ortho vs. para* states are determined by the sign of $(-1)^{\nu_3+K_a}$, and the parity of the states is determined by the sign of $(-1)^{K_c}$; thus, for the allowed transitions $\Delta\nu_3 + \Delta K_a$ is even and ΔK_c is odd. For D₂H⁺, the *ortho vs. para* states are determined by the sign of $(-1)^{\nu_3+K_a+K_c}$, and the parity of the

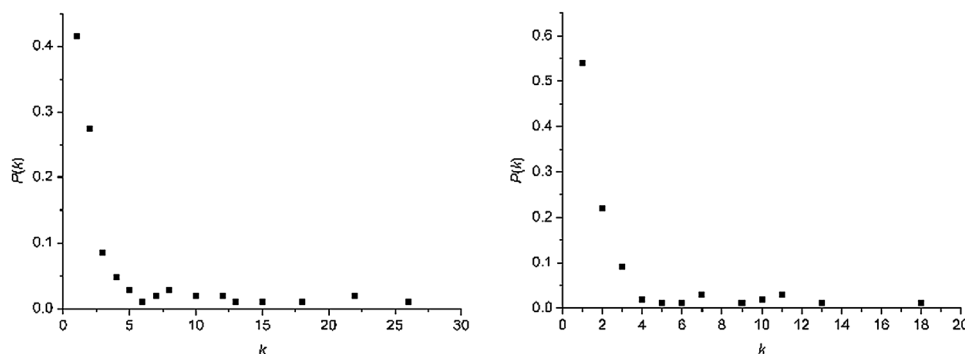


Fig. 5 Size–frequency [$k - P(k)$] distribution of the spectroscopic networks of H_2D^+ (left panel) and D_2H^+ (right panel).

Table 3 Symmetry characteristics of the $(\nu_1\nu_2\nu_3)_{K_aK_c}$ rovibrational states of H_2D^+ and D_2H^+ within the $C_{2v}(\text{M})$ molecular symmetry (MS) group^a

Γ_{rve}	H_2D^+				D_2H^+			
	ν_3	K_aK_c	Parity	SSW	ν_3	K_aK_c	Parity	SSW
A_1	e	e e	e	3	e	e e	e	12
	o	o e			o	o e		
A_2	e	e o	o	3	e	o o	o	12
	o	o o			o	e o		
B_1	e	o o	o	9	e	e o	o	6
	o	e o			o	o o		
B_2	e	o e	e	9	e	o e	e	6
	o	e e			o	e e		

^a Γ_{rve} = rovibronic symmetry species, SSW = spin statistical weight factors, e = even, o = odd. The convention is that the component of the spectroscopic network with the larger SSW is called *ortho*, while the other is called *para*. The parity of the rovibrational states for both H_2D^+ and D_2H^+ is defined by the sign of $(-1)^{K_c}$.

states is determined by the sign of $(-1)^{K_c}$; thus, for the allowed transitions both $\Delta\nu_3 + \Delta K_a$ and ΔK_c are odd.

4 Nuclear motion computations

The variational nuclear-motion computations of this study, aimed at augmenting the MARVEL analysis and providing important constraints and guidelines, were performed with the latest version of the D^2FOPI code,⁷⁴ employing Jacobi coordinates, an R_1 coordinate-frame embedding, and a mixed DVR (discrete variable representation) and FBR (finite basis representation) representation. For details on the protocol, see Section III and the ESI† of ref. 74. In order to cover some part of the nonadiabatic effect, different rotational and vibrational masses were employed, following the recommendation of Polyansky and Tennyson.⁷⁵ The rotational masses were chosen to be $m_{\text{rot,H}} = 1.007276$ u and $m_{\text{rot,D}} = 2.01355$ u, while the vibrational masses were set to $m_{\text{vib,H}} = 1.007537$ u and $m_{\text{vib,D}} = 2.01381$ u. All nuclear motion computations whose results are reported are converged to better than 0.01 cm^{-1} in the (ro)vibrational energies. For this, it was sufficient to employ 30 basis functions along each coordinate.

4.1 The PES

During the course of this work, there was a special effort to validate both the experimental transition wavenumbers and the

derived energy levels, including their labeling, *via* results obtained from first-principles nuclear motion computations. Therefore, the energy-level computations were based on high-level adiabatic potential energy hypersurfaces^{15,16} and exact and approximate quantum numbers and symmetries were determined from the nuclear motion computations of this study.

The average accuracy of the computed rovibrational transitions using these PESs is better than 0.05 cm^{-1} (Fig. 8 and 9, *vide infra*); therefore, experimental transitions which deviated more than 0.1 cm^{-1} from entries in the variational linelists with matching rotational quantum number J and parity, were checked carefully before processing them further by MARVEL.

4.2 RRD labeling

It is a strict requirement that the dataset of transitions employed in a MARVEL analysis contains a single unique assignment for each of the isotopologues, labeling both the lower and the upper states. Without this information the MARVEL inversion process from transitions to energies cannot be executed.

Thus, a model must be available prior to using MARVEL in order to give reasonable and unique labels for the experimental transitions. Approximate Hamiltonians as well as variational computations based on highly accurate potential energy surfaces, obtained perhaps *ab initio*,^{76–79} are able to provide these labels for most small semirigid molecules of interest. Of course, if more than one electronic state was considered, an extra label should be used to distinguish between these electronic states.

The “rigorous” labeling based on J and parity is a natural one for energy levels obtained from variational computations but of only limited usefulness when analysing experimental data. Thus, a procedure is needed which appends the rigorous quantum numbers with approximate ones based on the rigid rotor – harmonic oscillator approximation.

The rigid rotor decomposition (RRD) labeling scheme⁸⁰ was used in this study to provide rotational labels for the computed rovibrational states. RRD is based on the overlap of variationally computed rovibrational wavefunctions with functions obtained as a product of variational vibrational wavefunctions and rigid-rotor eigenfunctions. If the latter two have unique vibrational and rotational approximate quantum labels, the rovibrational states can be associated with a unique set of rovibrational quantum numbers based on the largest RRD overlaps. The unique vibrational

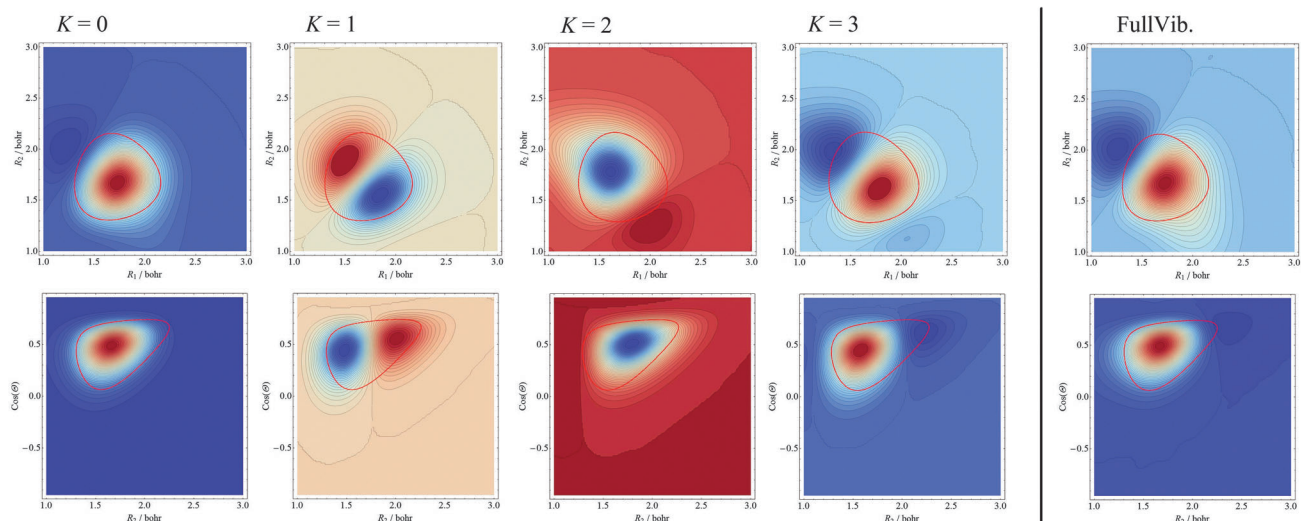


Fig. 6 Wavefunction plots for the pure rotational 3_{03} state of H_2D^+ , see the text for further details about the panels of the figure.

normal-mode labels ($\nu_1\nu_2\nu_3$) of H_2D^+ were taken from ref. 81 and by matching energies, which is straightforward for the low-energy pure vibrational states investigated. The rotational asymmetric top limit $J_{K_a K_c}$ labels were generated during the rigid-rotor computations following the standard rigid-rotor labeling scheme.¹⁸ The detailed description of the method of computing RRD tables can be found in ref. 74. For the rigid-rotor computations the rotational constants were chosen, in cm^{-1} , as 43.362, 29.143, and 16.610 cm^{-1} for H_2D^+ and 36.243, 21.869, and 13.057 for D_2H^+ .⁸² The same rotational constants are employed for all vibrational states considered.⁷⁴

Besides providing unique quantum labels, the RRD computations can also be used to deduce the symmetry of the rovibrational wavefunctions. For a given rovibrational state this can be done by determining the symmetry of the direct-product basis function which was used for its RRD labeling, which naturally has the same symmetry as the rovibrational wavefunction. For details see Section II of ref. 74.

The approximate quantum labels obtained in the RRD procedure, considering “full vibrational overlaps” (see Section II of ref. 74) along with the labels obtained simply from the three largest RRD overlaps, are given for all rovibrational states computed with $J \leq 7$ for the first 15 VBOs of H_2D^+ and D_2H^+ in the ESI† (ref. 71)) Where possible, the variational energy levels are augmented with the MARVEL ones of this study. It is suggested that the rovibrational labels provided in the ESI† (ref. 71) should be used in future assignments of experimental high-resolution spectra of H_2D^+ and D_2H^+ .

As to the RRD labels, it is important to note that the largest elements of the computed RRD tables for a given rovibrational state are always considerably larger for D_2H^+ than for H_2D^+ . This is connected to the fact that H_2D^+ is a much more asymmetric molecule than D_2H^+ . In order to investigate whether the considerable RRD differences are evident in the rovibrational wavefunctions, in Fig. 6 and 7 cuts along the

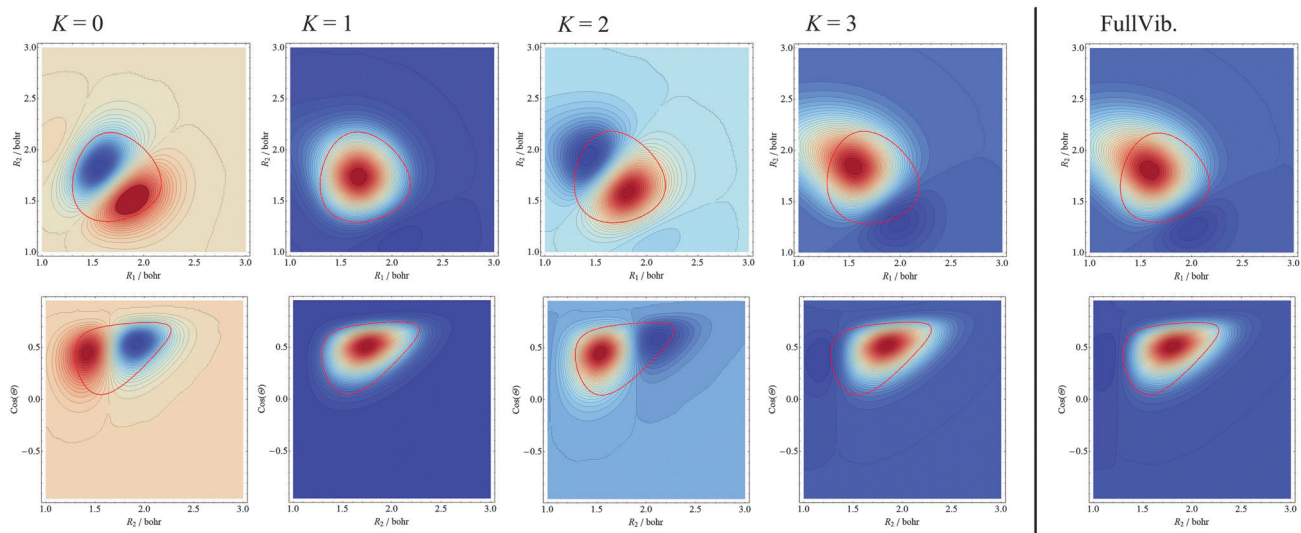


Fig. 7 Wavefunction plots for the pure rotational 3_{31} state of H_2D^+ , see the text for further details about the panels of the figure.

wavefunctions of the pure rotational 3_{03} and 3_{31} states of H_2D^+ , respectively, are presented. These two states have been chosen since for $(0\ 0\ 0)_{3_{03}}$ and $(0\ 0\ 0)_{3_{31}}$ the largest RRD coefficients are drastically different, 0.76 and 1.00, respectively. In the figures the different $K = 0, 1, 2, 3$ wavefunction components, corresponding to the different rotational basis functions, are plotted, as well as their sum, providing the final wavefunction, available at the rightmost part of the figures. In the upper row of the figures the HDH bond angle was fixed to 60° and thus it shows the wavefunction as the function of the two HD stretchings. In the lower row of the figures we fixed one of the two HD stretches at 2 bohr and the wavefunctions are plotted as a function of the cosine of the HDH angle and of the other HD stretch. These and similar wavefunction plots, not shown here, suggest that these RRD differences are not clearly visible in the wavefunction plots.

5 MARVEL energy levels

Tables 4 and 5 contain MARVEL vibrational band origins (VBO) determined for H_2D^+ and D_2H^+ , respectively. Due to the limited amount of available experimental information, only 6 and 5 excited vibrational states could be determined for H_2D^+ and D_2H^+ , respectively. All vibrational fundamentals are known for H_2D^+ , but one of them, ν_1 , remains experimentally unknown for D_2H^+ . The ν_1 VBO has been given before in the literature^{20,37,42,51} but introduction of “CD transitions” was necessary to obtain its value. Thus, it is not known experimentally in a strict sense. The MARVEL rovibrational energy levels determined are listed in Tables S1–S4 (ESI[†]), separated not only for the isotopologues but also for the *ortho* and *para* spin isomers.

An important step in the validation of the MARVEL energy levels is their checking against the results of variational nuclear motion computations. This step is of particular importance for

Table 4 MARVEL vibrational band origins (VBO), MARVEL uncertainties (Unc.), and the number of rotational levels (RL) the vibrational levels are holding within the present database of the H_2D^+ isotopologue^a

$\nu_1\nu_2\nu_3$	VBO	Unc.	RL
0 0 0	0.0000 ^b	0	20
0 1 0	2205.8772	50	15
0 0 1	2335.4260	50	21
1 0 0	2992.5042	17	22
0 2 0	—	—	4
0 1 1	—	—	3
0 0 2	—	—	1
0 3 0	6287.6672	50	4
0 2 1	6400.7110	50	9
1 2 0	6991.5782	50	7

^a The uncertainties are given in units of 10^{-4} cm^{-1} . The VBOs, given in cm^{-1} , are ordered according to their energies. To complete the list of VBOs up to 7000 cm^{-1} , the VBOs $(1\ 1\ 0)$, $(1\ 0\ 1)$, and $(2\ 0\ 0)$ must be added in between the $(0\ 0\ 2)$ and $(0\ 3\ 0)$ VBOs, *i.e.*, between 5200 and 6000 cm^{-1} . The $(0\ 0\ 3)$ VBO has about the same energy as the $(1\ 2\ 0)$ VBO. These VBOs are not listed as no corresponding rovibrational energy levels were involved in the measured transitions. ^b The value of the vibrational ground state was fixed to zero with zero uncertainty. The variational computation of this study yields the value of 4071.46 cm^{-1} for the zero-point vibrational energy.

Table 5 MARVEL vibrational band origins (VBO), MARVEL uncertainties (Unc.), and the number of rotational levels (RL) the vibrational levels are holding within the present database of the D_2H^+ isotopologue^a

$\nu_1\nu_2\nu_3$	VBO	Unc.	RL
0 0 0	0.0000 ^b	0	17
0 1 0	1968.1620	100	20
0 0 1	2078.4300	100	18
1 0 0	—	—	22
0 2 0	—	—	4
0 0 2	4042.7722	90	6
0 1 1	4060.7884	140	5
1 2 0	—	—	1
1 0 2	—	—	6
1 1 1	6616.0270	50	1

^a The uncertainties are given in units of 10^{-4} cm^{-1} . The VBOs, given in cm^{-1} , are ordered according to their energies. The VBOs $(1\ 1\ 0)$, $(1\ 0\ 1)$, $(2\ 0\ 0)$, $(0\ 3\ 0)$, $(0\ 0\ 3)$, $(0\ 2\ 1)$, and $(0\ 1\ 2)$ between 4640 and 6010 cm^{-1} , in between the $(0\ 1\ 1)$ and $(1\ 2\ 0)$ VBOs, are not listed in this table as no corresponding rovibrational energy levels have been detected experimentally. ^b The value of the vibrational ground state was fixed to zero with zero uncertainty. The variational computation of this study yields the value of 3635.55 cm^{-1} for the zero-point vibrational energy.

levels determined by a single transition or for those levels which are part of a series of levels interconnected by single transitions. Any rovibrational MARVEL level obtained as part of this work which differed by more than 0.025 cm^{-1} from its variational counterpart was subject to further scrutiny. At the same time the transitions were checked for consistency as the difference between observed and calculated levels generally shows great regularity as J varies for a given vibrational state and values of K_a and K_c . The appropriate comments to Table 1 list the only two transitions removed at this stage from the MARVEL analyses.

In order to highlight the utility of the variational linelists, differences between our whole MARVEL energy level dataset and the corresponding rovibrational levels computed variationally are plotted in Fig. 8 and 9. As clear from these figures, none of the differences are substantial, even at as high energies as 7000 cm^{-1} , and they mostly arise from the discrepancies between the measured and computed VBOs. Thus, the predictive power of the computations is considerably better for the rotational–vibrational lines if this discrepancy is taken into account. Note that most of the (observed – computed) differences are of the same sign, this suggests that consideration of nonadiabatic effects is still not optimal, as also noted before.¹⁵

5.1 H_2D^+

While there are scattered MARVEL energies available for 10 VBOs of H_2D^+ , the coverage of rovibrational levels is complete up to $J = 3$ only for the $(0\ 0\ 0)$, $(0\ 0\ 1)$, and $(1\ 0\ 0)$ VBOs. Our understanding of the rotational states of the $(0\ 1\ 0)$ VBO is complete up to $J = 2$. For all the other VBOs and J values the energy level information is highly incomplete. There are only a few rovibrational levels with $J = 6$ or 7 and none with higher rotational excitation. In fact, as shown on Fig. 1–4, the $J = 7$ rotational–vibrational levels are part of FCs and thus these energy levels are not determined in an absolute sense by MARVEL.

MARVEL gives the most dependable results when a particular energy level is at the center of a network of many transitions

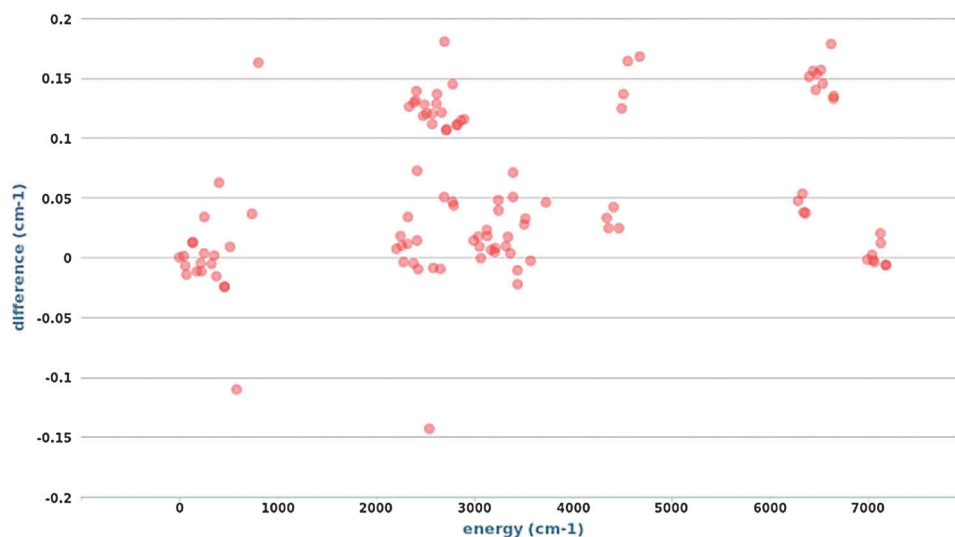


Fig. 8 Differences, in cm⁻¹, between the present MARVEL energy levels and their variationally obtained counterparts for H₂D⁺ (an interactive version of this figure with pop-up labels and a zoom-in facility is available in the ESI† (ref. 71) to this paper).

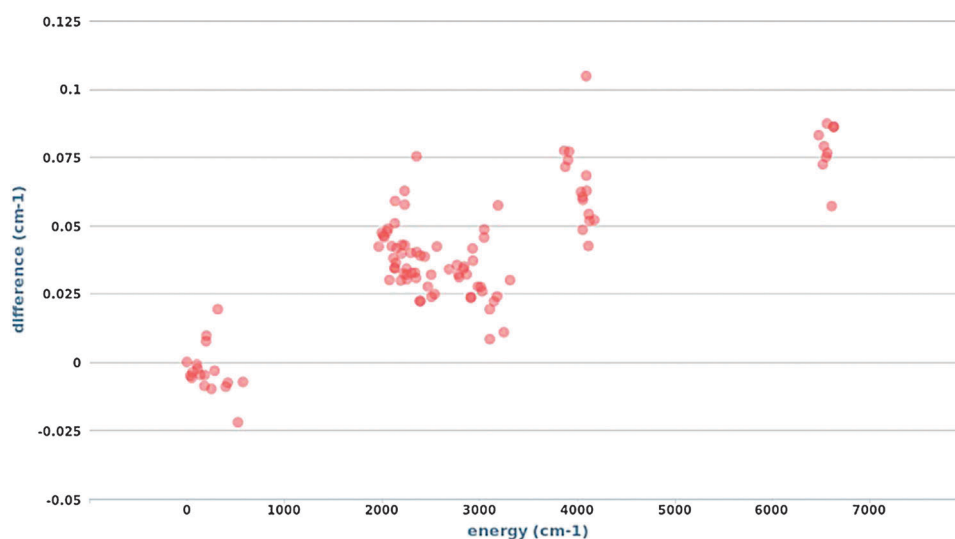


Fig. 9 Differences, in cm⁻¹, between the present MARVEL energy levels and their variationally obtained counterparts for D₂H⁺ (an interactive version of this figure with pop-up labels and a zoom-in facility is available in the ESI† (ref. 71) to this paper).

containing several circles. Inevitably, there are always energy levels which are linked to the main network by a single transition, indeed in the case of branches there may be a series of such transitions. For these levels MARVEL can neither confirm the reliability of the experimental assignment nor give any reasonable uncertainty value if there are problems (for example, misrepresentation, misassignment, or mislabeling) with the experiment.

The agreement between the variationally determined and the MARVEL energy levels is excellent, especially after taking into account the discrepancies between the two sets of VBOs. The average deviation is less than 0.02 cm⁻¹, close to the intrinsic precision of the computed rovibrational levels. Therefore, the “sizable” deviations, on the order of 0.1 cm⁻¹, for the

(0 1 0) *4*₁₄, (0 0 0) *4*₂₂, and (0 0 1) *4*₁₄ levels suggest problems with these MARVEL energy levels and the underlying transitions. These transitions are left in the MARVEL analysis but the use of these energy levels in the analysis of spectra is discouraged. To call attention to this problem these MARVEL energy levels are printed in italics in Tables S1 and S2 of the ESI†

The pure rotational spectrum of H₂D⁺ is particularly relevant for astrochemistry but only a few transitions have been observed in the laboratory. The 372.4 GHz line of *ortho*-H₂D⁺, corresponding to the pure rotational transition *1*₁₀–*1*₁₁, has been measured several times,^{38,39,45} most accurately by Amano and Hirao.⁴⁵ This transition has been considered as a probe for the presence of dark matter⁸³ and thus its precise position is highly relevant. Despite the fact that both energy levels are hubs

within the SN and are parts of several circles, MARVEL can not help to determine an even more reliable transition wavenumber than measured in the best experiment.

Asvany and co-workers⁴⁹ determined, using action spectroscopy, the lowest-lying $1_{01} \leftarrow 0_{00}$ transition of *para*-H₂D⁺ with a line center frequency of 1370 084.880(20) MHz. The previous value of this transition reported by Amano and Hirao,⁴⁵ but not measured by them, is incorrect, see the related discussion by Asvany *et al.*,⁴⁹ and thus was not included in the MARVEL analysis.

5.2 D₂H⁺

Unlike in the case of H₂D⁺, for the D₂H⁺ isotopologue all the MARVEL energy levels match closely their variational counterparts. The average deviation is again less than 0.02 cm⁻¹, suggesting that the variational rovibrational levels, at least for the lower VBOs investigated here, could easily guide the assignment process of new measurements involving these states.

Several publications investigated the energy levels of D₂H⁺.^{28,43,52} In particular, Alijah and Beuger²⁸ computed term values of the 11 lowest vibrational states with *J* values up to *J* = 10. They also tried to determine labels for their computed rovibrational states, the procedure employed by them is described in ref. 81. Since in this study we also determined labeled rovibrational energies employing a considerably more accurate variational treatment (we employ a more accurate PES and take into consideration nonadiabatic effects neglected in ref. 28), it is worth comparing the results of the two studies. Agreement between the energy levels is as good as can be expected. For the trivial assignments made by Alijah and Beuger for low vibrational and rotational energies the two studies are also in agreement. For example, there are no differences for the (0 0 0) VBO, there is only one disagreement, for 7₆₁, for the (1 0 0) VBO (here the largest RRD coefficient is larger than 0.5 ensuring that the present, RRD-driven label is the correct one). Similarly, there is only one disagreement for the (2 0 0) VBO, for 5₂₄, and here again the RRD label should be correct. There are three disagreements for the (0 2 0) VBO, those for 4₃₂, 5₄₁, and 6₄₂. For the first level the RRD label is secure while for the other two it is most likely correct. For some of the higher-lying states, especially those in Coriolis coupling, like (0 1 0)/(0 0 1), (0 0 2)/(0 1 1), and (1 1 0)/(1 0 1), there are a few expected disagreements, for example, altogether 8 for the (1 1 0)/(1 0 1) pair. The only energy level where the RRD table does not yield a secure label is (0 1 0) 7₃₅, where the mixing is so strong that a physically correct label cannot be given.

6 New assignments

As for many other molecules, for H₂D⁺ and D₂H⁺ there are several measured lines reported in the literature without labels attached. For example, Polyansky and McKellar,⁵² after their improved analysis of the then available experimental data, left eight and four lines unassigned for H₂D⁺ and D₂H⁺, respectively. Furthermore, there are several lines in the PhD thesis of Shy⁸⁴ which remained unlabeled over the last 30 years

Table 6 Proposed new assignments, based on rovibrational energy levels from variational nuclear motion computations, RRD tables and the available MARVEL vibrational band origins for H₂D⁺

Source	Measured wavenumber	Variational result	Suggested labeling
90PoMc ^{a,52}	1995.953	1995.99	(0 3 0) 3 ₃₁ ← (0 2 0) 3 ₃₀
	2134.930	2134.84	(0 1 1) 6 ₂₄ ← (0 1 0) 6 ₃₃
	2274.932	2274.94	(0 0 2) 8 ₂₇ ← (0 1 0) 8 ₂₆
	2302.478	2302.57	(1 0 1) 2 ₂₀ ← (1 0 0) 2 ₁₁
82Shy ^{b,84}	1934.196	1934.12	(0 2 0) 4 ₁₄ ← (0 1 0) 5 ₁₅

^a These lines were observed by Foster *et al.*^{20,42} but not reported in the original papers. Polyansky and McKellar,⁵² who performed a careful reanalysis of all the experimental results available prior to 1990, left eight lines unassigned. ^b Two unlabeled lines reported for H₂D⁺.

Table 7 Proposed new assignments, based on rovibrational energy levels from variational nuclear motion computations, RRD tables and the available MARVEL vibrational band origins for D₂H⁺

Source	Measured wavenumber	Variational result	Suggested labeling
90PoMc ^{a,52}	2034.113	2034.14	(0 2 0) 7 ₁₆ ← (0 1 0) 6 ₂₅
82Shy ^{b,84}	1878.1995	1878.16	(0 0 1) 4 ₃₂ ← (0 0 0) 5 ₃₃
	1882.1577	1882.14	(0 1 0) 3 ₀₃ ← (0 0 0) 3 ₁₂
	1964.2472	1964.31	(0 2 0) 3 ₂₂ ← (0 1 0) 3 ₁₃

^a These lines were observed by Foster *et al.*^{20,42} but not reported in the original papers. Polyansky and McKellar,⁵² who performed a careful reanalysis of all the available experimental results prior to 1990, left four lines unassigned. ^b There are 13 unlabeled lines reported for D₂H⁺.

for these ions. After the execution of the MARVEL analysis and having accurate variational rovibrational energy levels and RRD tables at our disposal, it was attempted to assign labels to these measured lines. Somewhat unexpectedly, this proved to be a difficult task.

None of the unlabeled measured lines could be labeled based on the MARVEL energy levels. The available variational data, due to their considerable accuracy, provides the next resource to label these lines. During the present study the assignment is helped by the available MARVEL VBOs as the computed rovibrational states acquire most of their error from the “displacement” of their VBO. Thus, these discrepancies can be corrected straightforwardly. The principal remaining problem is that for several lines there are quite a few computed transitions which agree with them within much better than 0.1 cm⁻¹, our criterion to identify possible candidates for the lower and upper energy levels. The extremely dense coverage provided by the computed transitions thus hinders the selection procedure. An additional difficulty is that although there is a computed linelist available for H₂D⁺ with computed one-photon intensities, there is no such linelist for D₂H⁺. Furthermore, some of the measurements do not correspond to this type of absorption experiment. Nevertheless, as Tables 6 and 7 demonstrate, some of the unlabeled lines can still be labeled based on our variational results (energy levels and RRD tables). Nevertheless, since these assignments should be confirmed experimentally, they were not included in the MARVEL analysis of the present study.

7 Summary and conclusions

Among the species for which detailed and accurate spectroscopic data are needed for important scientific and engineering applications, including details of the chemistry of cold and warm interstellar media, the isotopologues of H_3^+ hold a central place. Thus, the study of their spectra is of widespread interest. At the same time, the task of obtaining and understanding high-resolution spectra, often at different temperature regimes, provides a fertile testing ground for different experimental and theoretical approaches yielding the required information (line positions, intensities, and shapes). It would be convenient if high-resolution molecular spectroscopy experiments could yield the line-by-line information required for the many applications of the spectroscopic data. However, while experiments often yield accurate data, the amount of information that can be obtained is only a small fraction of that required, as proven in this study once again. Quantum theory, on the other hand, can result in the full information^{60,85} but the accuracy of even the most sophisticated treatments¹⁵ is considerably worse for polyatomic systems, especially for line positions, than that of experiments. Therefore, the best possible approach one can take is to use all the available experimental and quantum chemical information to come up with a linelist as accurate as allowed by the available data.

In this study we employed the MARVEL (Measured Active Rotational–Vibrational Energy Levels) scheme^{60,61,69} and obtained accurate rovibrational energy levels for the H_2D^+ and D_2H^+ isotopologues of the molecular ion H_3^+ . The MARVEL approach, especially when combined with results from sophisticated variational nuclear motion computations, provides an ideal platform to achieve the goal of determining accurate rovibrational energy levels from which precise line positions can be calculated straightforwardly. The MARVEL analysis is based on the concept of spectroscopic networks (SN).^{67,68} The components of the experimental SNs of the two isotopologues, despite the fact that they are based on only a limited amount of information, show the repeatedly observed scale-free behavior, allowing the identification of hubs within the SNs. The number of critically evaluated and recommended experimental (levels, lines) for H_2D^+ and D_2H^+ are (109, 194) and (104, 155), respectively (Table 8).

Accuracy (and precision) of the energy levels determined in this study is dependent upon several factors. Most important among these is the accuracy of the observed transitions. Although our analysis utilized all available experimental information, there are only a few energy levels which are involved in

multiple transitions measured by different experimental groups utilizing different spectrometers and experimental conditions. Thus, uncertainties of some of the levels are probably optimistic, especially if they come from a single source.

Over the course of the present study it became clear that determination of an accurate set of energy levels requires not only dependable experimental data but also a first-principles approach to determine as accurate energy levels as possible. This was provided here by variational nuclear motion computations employing the most accurate adiabatic PESs of H_2D^+ and D_2H^+ . Besides the accurate computed energy levels the wavefunctions obtained were analyzed based on the rigid-rotor decomposition (RRD) scheme, yielding dependable rigid-rotor labels for the levels. These labels helped to validate, and correct in a few cases, the labels of the rovibrational energy levels of H_2D^+ and D_2H^+ available in the literature. The lists of assigned MARVEL and variational lines and levels obtained for H_2D^+ and D_2H^+ as part of this study are deposited in the ESI† to this paper.

Acknowledgements

The authors would like to thank the Scientific Research Fund of Hungary (OTKA grant no. NK83583) for generous support of the research described. The authors thank Mr Amir Garmarudi and Mr István Szabó for their help with data collection at an early stage of the project. Useful discussion with Dr Oskar Asvany (Köln, Germany) are gratefully acknowledged.

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Table 8 Summary of the energy levels determined for the H_2D^+ and D_2H^+ isotopologues during the present study^a

SN component	H_2D^+	D_2H^+
Para	46	52
Ortho	63	52
FC	14	27
Sum	123	131

^a SN = spectroscopic network, FC = floating component (see text).

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