Microwave spectrum of the H2DO+ion: Inversion-rotation transitions and inversion splitting

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Microwave spectrum of the H_2DO^+ ion: Inversion-rotation transitions and inversion splitting

Takashi Furuya, Shuji Saito,[a] and Mitsunori Araki[b]
Research Center for Development of Far-Infrared Region, University of Fukui, Bunkyo, Fukui 910-8507, Japan

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Inversion-rotation spectral lines of the monodeuterated hydronium ion, H_2DO^+, have been observed by a source-modulation spectrometer in the millimeter- to submillimeter-wave region. The ion was generated by a hollow-cathode discharge in a gas mixture of H_2O and D_2O. Nine inversion-rotation lines were measured precisely for the lowest pair of inversion doublets in the frequency region from 210 to 720 GHz. The measured lines were analyzed to derive rotational constants in the inversion-doublet states and inversion splitting. The inversion splitting in the ground state was determined to be 1 215 866(410) MHz, that is, 40.5569(137) cm^{-1}, where the numbers in parentheses give probable uncertainties estimated from the Jacobian matrix of the assumed centrifugal distortion constants of the inversion-doublet states. The determined inversion splitting is off by −0.58 cm^{-1} from the predicted value of 41.14 cm^{-1} by Rayamäki *et al.* using high-order coupled cluster *ab initio* calculations [J. Chem. Phys. **118**, 10929 (2003)], and by 0.039 cm^{-1} from the observed value of 40.518(10) cm^{-1} by Dong and Nesbitt using high-resolution jet-cooled infrared spectroscopy [J. Chem. Phys. **125**, 144311 (2006)] beyond the quoted uncertainty. The most astronomically important transition 0_{00}^{-}-1_{0}^{+} for the *ortho* species was measured at 673 257.024(31) MHz, which could be used as a radioastronomical probe investigating interstellar chemistry of deuterium fractionation in space. © *2007 American Institute of Physics.*
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I. INTRODUCTION

Molecular ions have been known to be essential in gas-phase interstellar chemistry which is deeply related to physical evolution processes of molecular clouds to stars. So far only 14 molecular ions have been identified in space from radio telescope observations. The protonated water ion, H_3O^+, is the precursor of H_2O and OH in space and is produced by protonation of oxygen atom by H_3^+ and successive hydrogen-atom abstraction from H_2.[1] The low H_2O abundance in space has been a longstanding puzzling problem and the recent submillimeter wave astronomy satellite observations[2] of interstellar water suggested a close relation between gas-phase ion-molecule reactions and dust surface reactions.[3] A direct observation of interstellar spectral lines of H_3O^+ had been expected so as to probe H_2O chemistry in space. Using precise line frequencies[4,5] measured in the laboratories, Wootten *et al.*[6] and Phillips *et al.*[7] identified low-lying submillimeter-wave lines towards giant molecular clouds after preliminary observations[8,9] of single lines. The monodeuterated species of H_3O^+, H_2DO^+, has attracted much interest in recent years because singly deuterated species of simple interstellar molecules such as H_2CO, NH_3, and CH_3OH have been detected in hot cores of giant molecular clouds and in cold dark cloud cores showing high deuterium fractionation.[10] Furthermore, even multiply deuterated species have been identified in similar astronomical sources.[11–13] This high deuterium fractionation has been rationalized as a result of CO depletion in dark cloud cores.[14,15] Recently, it is suggested that, similar to NH_3 and N_2H^+ in the extremely highly depleted cores, OH, H_2O, and H_3O^+ may survive in the gas phase in highly depleted cores if atomic oxygen does not stick efficiently to grain surfaces.[16,17] The spectral lines of deuterated H_3O^+ should be searched in such highly depleted cores. We have provided the laboratory line frequencies of H_2DO^+ for this search.

The H_3O^+ ion is one of the most fundamental molecular ions in various fields and its first high-resolution spectroscopic studies started in infrared region in 1983–1984. The ν_3 infrared band of H_3O^+ was first observed by Begemann *et al.*[18] using a color center laser spectrometer combined with velocity modulation and the ν_2 band by Haese and Oka[19] with a diode laser spectrometer. Like its isoelectronic counterpart, NH_3, H_3O^+ is a pyramidal molecule with inversion but the inversion splitting has been found to be much higher at 55.3462(55) cm^{-1}.[20] The infrared spectra have been studied extensively by several research groups[21–33] reporting its detailed molecular constants such as band origins, inversion splittings, and rotational and centrifugal distortion constants. The large splitting brings about only five submillimeter-wave transitions below 1 THz. Plummer *et al.*[4] and Bogey *et al.*[5] measured four inversion-rotation transitions of H_3O^+ in the laboratory, guided by the molecular constants from the infrared studies. Verhoeve *et al.*[34] used a far-infrared sideband laser spectrometer to extend measurements to the far-infrared

[a]Electronic mail: ssaito@cyber.ocn.ne.jp.
[b]Present address: Department of Chemistry, Sophia University, Chiyoda-ku, Tokyo 102-8554, Japan.

region and determined the inversion splitting to be 55.349 98(4) cm^{-1}. Several inversion-rotation transitions of D_3O^+ were studied by submillimeter-wave spectroscopy and the inversion splitting was determined to be 15.355 503 37(107) cm^{-1} [Araki *et al.* 1998 (Ref. 35) and 1999 (Ref. 36)].

The H_3O^+ ion has been a challenging target also for quantum chemical calculation[37–43] and its potential surface has been calculated to predict vibrational and rotational levels and equilibrium structure. However, only a few calculations have been carried out on the molecular properties of the isotopic species. Daniels and Spirko[40] fitted a model potential function of H_3O^+ to the *ab initio* calculation data[37] and predicted inversion splittings and ν_2 mode levels of four isotopic species: the inversion splitting of H_2DO^+ was calculated to be 40.1 cm^{-1}. Huang *et al.*[42] presented vibrational levels including inversion splittings for H_2DO^+ and HD_2O^+ from a new potential energy surface for H_3O^+ calculated by the CCSD(T) method with an aug-cc-pVQZ basis. The calculated inversion splitting of H_2DO^+ in the ground vibrational state was 34 cm^{-1} which was appreciably different from the value predicted by Daniels and Spirko.[40] Rajamäki *et al.*[43] calculated a six-dimensional potential energy surface for H_3O^+ using the CCSD(T) method with large basis sets and predicted the r_e structure of H_3O^+, vibrational levels, and inversion splittings of six isotopic species: 41.14 cm^{-1} for the inversion splitting of H_2DO^+.

The latest high-level calculation proposing sub-wavenumber accuracy for the inversion splittings[43] urged laboratory high-resolution spectroscopy. The first infrared jet-cooled spectra of HD_2O^+ were studied by Dong *et al.*[44] who observed both *b*-type and *c*-type bands of the ν_3 mode and determined detailed molecular constants. Very recently, they applied the same method to H_2DO^+ and measured *b*-type bands of the ν_3 mode and *a*-type and *c*-type bands of the ν_1 mode.[45] They reported rotational constants for doublet pairs of the ground, $\nu_1=1$, and $\nu_3=1$ states and $\nu_1 \leftarrow 0$ and $\nu_3 \leftarrow 0$ band origins. They also determined the inversion splitting of the ground state from the observed $\nu_1^- \leftarrow 0^+$ and $\nu_1^- \leftarrow 0^-$ bands to be 40.518(10) cm^{-1}.

II. EXPERIMENT

A. Molecular constants

Since H_2DO^+ is a light asymmetric molecule, a prediction of reliable molecular constants is vital to significant reduction of searching times for lines sufficient for their assignment. When one of three hydrogens of H_3O^+ is replaced by a deuterium atom, the *c* principal axis of the H_3O^+ symmetric top rotates by 6.7° in the *ac* plane and the center of the gravity of the deuterated species moves by 0.0485 Å from the center of electric charge in H_3O^+. The shift of the center of the gravity in H_2DO^+ induces a dipole moment of 0.23 D. If the dipole moment of H_3O^+ is assumed to be 1.4 D,[46] the total dipole moment of H_2DO^+ becomes 1.34 D and its direction rotates by −9.6° from the *c* axis of H_3O^+ in the *ac* plane. This gives the resultant μ_a component of 0.37 D to H_2DO^+ so that its *a*-type transition has one-thirteenth intensity of the *c*-type ones. As given later, observed signal to noise ratios of the *c*-type spectral lines of H_2DO^+ were not enough to identify the weak *a*-type transition lines.

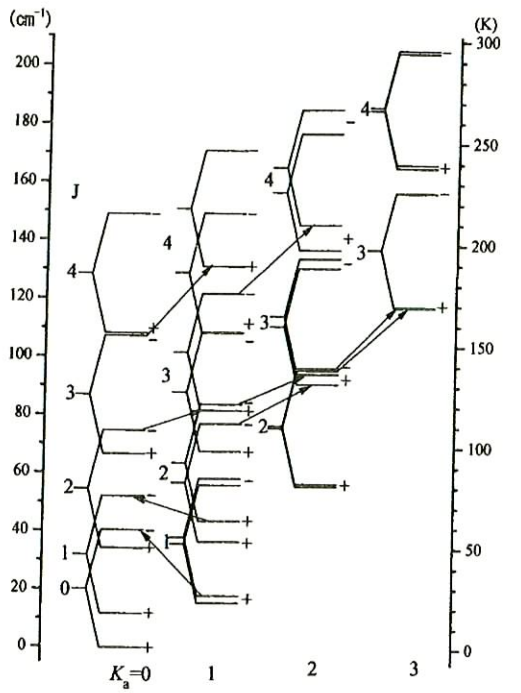

FIG. 1. Energy level diagram of H_2DO^+ indicating the observed submillimeter-wave transitions with full upward lines. Six observed lines with $K_a=1-0$ or 3–2 for *ortho* species and three with $K_a=2-1$ for *para* species.

The H_2DO^+ molecule has a plane of symmetry so that rotational levels within the state having the same parity are classified into two species: the K_a=odd rotational level combines with the *ortho* species for the hydrogen nucleus spin weight of 3 and the K_a=even level with the *para* species for the weight of 1 for the ground symmetric (0^+) state and *vice versa* for the ground antisymmetric (0^-) state. The inversion-rotation transitions obey the *c*-type selection rule for the levels of the same spin species between the ground tunneling doublet, which is indicated in Fig. 1. This shows that an energy level diagram of H_2DO^+ has an asymmetric prolate-top level structure modified by inversion doubling. Hence, frequencies of inversion-rotation transition of H_2DO^+ depend mainly on the rotational constants of both the ground tunneling doublet states and the inversion splitting of the ground state.

1. Rotational constants

The rotational constants of H_2DO^+ for the ground doublet state are calculated from assumed r_z structures for the ground symmetric state (0^+) and antisymmetric state (0^-), which are transferred from the previously reported r_z structures of H_3O^+ and D_3O^+.[36] The HO and DO bond lengths are assumed to be the corresponding bond lengths of H_3O^+ and D_3O^+, respectively, the bond angle of HOH to be the HOH

angle of H_3O^+, and that of HOD to be an average of the HOH and DOD angles of H_3O^+ and D_3O^+, respectively. The r_z rotational constants calculated from the combined r_z structures of H_3O^+ and D_3O^+ are corrected to the effective rotational constants by referring to changes between the B_0 and B_z constants of H_3O^+ and D_3O^+: for the 0^+ state, $A=329\,000\pm3300$, $B=212\,000\pm2100$, and $C=141\,000\pm1400$ MHz, and the 0^- state, $A=324\,000\pm3200$, $B=210\,000\pm2000$, and $C=142\,000\pm1400$ MHz, where uncertainties are assumed to be 1% of the constant. In the nearly final period of the line assignment process, Dong and Nesbitt[45] reported the molecular constants of H_2DO^+ determined from their jet-cooled IR spectroscopic study, which supported our experiment to some extent. Their and our observed molecular constants are compared later in Table II.

2. Centrifugal distortion constant

The H_2DO^+ ion is a light molecule for which centrifugal distortion effect makes a considerable contribution to rotational energy levels. An assumption of the centrifugal distortion constants is also important to adjust frequency ranges to be looked for. However, a set of plausible centrifugal distortion constants was not available in the beginning of the experiment. Since $(B+C)/2$ of the predicted rotational constants is calculated to be about 176 500 MHz, similar to the B_0 constants of D_3O^+,[36] the Δ_J constants of the 0^+ and 0^- states are assumed to be 8.54 and 7.57 MHz, respectively. The Δ_{JK} and Δ_K constants are assumed to be scaled values from the Δ_{JK} and Δ_K constants of NH_2D,[47] which is one of rare light asymmetric molecules showing inversion doubling. Contributions to transition frequencies by δ_J and δ_K are considered to be small and are neglected.

3. Inversion splitting

On the basis of the high-level *ab initio* calculation, Rajamäki *et al.*[43] predicted the tunneling splitting of H_2DO^+ in the ground inversion state to be 41.14 cm^{-1}. They also reported those of H_3O^+ and D_3O^+ to be 56.02 and 15.79 cm^{-1}, which differ by 0.67 and 0.43 cm^{-1}, respectively, from the observed values.[34,36] Since the inversion splitting is approximately proportional to the vibrational bending frequency and a function of the reduced mass for the inversion motion,[48,49] we made a correction on the predicted value for H_2DO^+ by using a simple empirical expression of $\nu_{inv}=\pi\nu_0(a\mu^2+b\mu+c)$, where ν_{inv} is the inversion splitting, ν_0 the bending vibrational frequency, and μ the reduced mass related to inversion motion. The ν_0 value for four isotopic species is assumed to be the bending frequency predicted by the *ab initio* calculations.[43] First, three parameters, a, b, and c, were determined to fit the calculated inversion splittings of four deuterated species[43] and, then, two of the three parameters were adjusted to cancel the observed deviations from the *ab initio* values for H_3O^+ and D_3O^+.[43] The corrected value derived was 40.55 ± 0.02 cm^{-1} for the ground state inversion splitting of H_2DO^+, where the uncertainty was estimated from changes in the derived values among choices for two parameters.

B. Spectroscopy

The submillimeter-wave spectrometer previously reported[50] was used to observe spectral lines of H_2DO^+. The molecular ion was produced by a hollow-cathode discharge in a gas mixture of H_2O and D_2O in a 2 m free-space Pyrex cell of 10 cm in diameter. When two strong lines at 633 and 650 GHz were definitely assigned as described later, partial pressures of H_2O and D_2O were adjusted to give optimum line intensity: 2.4 Pa of H_2O and 1.6 Pa of D_2O. A 1.1 m stainless-steel tube was used as the hollow cathode. The discharge current in line-search experiments was normally set at 400 mA. The cell temperature was kept around 240 K. So as to identify detected lines to be due to H_2DO^+, several examinations were made for each line having reasonable intensity. First, candidate lines were subjected to examinations to see whether they had transient lifetimes and were sensitive to a magnetic field of 60–90 G applied to the cell.[51] They should give no signals when the flow of H_2O or D_2O was cut off or when the cell temperature was cooled down below 200 K. When relative partial pressures of H_2O and D_2O were changed from 3:2 to 3:1, a large decrease in intensity must be observed for candidate lines. Finally, candidate lines should show a reasonable increase in intensity when extended negative glow discharge was obtained in the cell with a high magnetic field.[52]

The first line-search experiment was made in 1998 at the Institute for Molecular Science without a promising result for the 1^-_{01}-2^+_{11} transition in 263–283 GHz based on molecular constants available at that time.[33,40] This line-search experiment was further continued in Fukui University by adding a frequency region from 235 to 263 GHz on the basis of a new prediction using the r_z structures for H_3O^+ and D_3O^+, as discussed above. A promising line for the 1^-_{01}-2^+_{11} transition was found at 250.91 GHz, and a line assignable to the 3^+_{12}-2^-_{02} transition at 211.11 GHz from the 204.1–220.5 GHz line-search experiment. However, these two lines showed low signal to noise ratios and their assignments were not certain. A substantial progress was made when a pair of transitions, 3^+_{30}-2^-_{20} and 3^+_{31}-2^-_{21} (K_a-type doubling), were detected at 632.90 and 649.65 GHz, respectively, after a search in the 601–637 and 644–656 GHz regions. This definite assignment of the two strong lines resulted in finding the important 0^-_{00}-1^+_{10} transition at 673.26 GHz and, furthermore, confirmed the assignment of the 250.91 and 211.11 GHz lines. Detections and assignments of other weaker lines followed after the initial assignment and successive refinements of molecular constants using newly assigned lines with the more reliable predictions discussed above. In total, six lines of the *ortho* species and three lines of the *para* species were detected and assigned in 210–720 GHz, as indicated in Fig. 1. The most astronomically interesting one among the observed spectral lines, the 0^-_{00}-1^+_{10} transition, is shown in Fig. 2. Each line frequency was determined by averaging five pairs of upward and downward frequency sweep measurements. The observed frequencies include ion-drift Doppler shifts of 40–130 kHz.[35] The ion-drift corrected frequencies are listed in Table I.

FIG. 2. The 0^-_{00}-1^+_{10} transition of the H_2DO^+ ion, observed with an integration time of 40 s. The ion was produced by a 400 mA dc discharge in a gas mixture of H_2O (2.4 Pa) and D_2O (1.6 Pa) at the cell temperature of 240 K.

C. Analysis

The nine measured line frequencies were analyzed using the standard Hamiltonian of an asymmetric top for both the 0^+ and 0^- states with the inversion splitting. The observed line frequencies were fitted to give three rotational constants of each doublet state, inversion splitting, and Δ_{JK} and Δ_K centrifugal distortion constants for the 0^+ state. The Δ_J constant was assumed to be 8.54 and 7.57 MHz for the 0^+ and 0^- states, respectively. The Δ_{JK} and Δ_K constants for the 0^- state were set to be in proportion to those of the 0^+ state by a factor of 0.886, which is the ratio between the Δ_J constants of the states.[36] The δ_J and δ_K constants were neglected in the analysis. The determined molecular constants are listed in Table II. Listed uncertainty of the determined molecular constant is estimated from Jacobian factors for the constant when the fixed Δ_J constants are changed by ±20% and the ratios of the Δ_{JK} and Δ_K constants between the 0^+ and 0^- states by ±20%, which are considered to represent the maximum changes of the molecular constants determined from a small number of observed inversion-rotation lines.

III. DISCUSSIONS

Among 14 inversion-rotation lines of H_2DO^+ having transition frequencies less than 750 GHz with $J \leq 5$ and $K_a \leq 3$, nine relatively strong lines were identified and measured precisely. The most interesting and important *ortho* species line among them is the 0^-_{00}-1^+_{10} transition at 673 GHz, as indicated in Fig. 1 and shown in Fig. 2. This line is located at the midst of the 600 GHz window of atmospheric interference and the precisely measured frequency of 673 257.024(31) MHz can be used for astronomical observations from ground-based radio telescopes. The upper level of this transition is located at 58 K above the ground level so that the core sources to be looked for should have relatively high temperature as found in hot cores of giant molecular clouds. The most important transitions of the *para* species are the 1^-_{10}-0^+_{00} and 1^-_{11}-1^+_{01}, which are located at 1.75 and 1.33 THz, respectively, and will be looked for high excitation sources of about 80 K with space telescopes. Other important transitions of both species are located in the terahertz region, as shown in Fig. 1. Laboratory high-resolution far-infrared spectroscopy is expected to supply precise transition frequencies in terahertz region and improve molecular constants including detailed centrifugal distortion constants for H_2DO^+.

TABLE I. Inversion-rotation transition frequencies of H_2DO^+ (MHz).

$J'_{Ka'Kc'}-J_{KaKc}$	$\nu_{obs.}$[a]
$0^-_{00}-1^+_{10}$	673 257.024(31)
$1^-_{01}-2^+_{11}$	250 914.101(13)
$3^+_{12}-2^-_{02}$	211 108.801(10)
$4^+_{3}-3^-_{03}$	716 959.392(70)
$3^+_{21}-2^-_{11}$	312 831.805(62)
$3^+_{22}-2^-_{12}$	412 130.206(71)
$4^+_{22}-3^-_{12}$	715 827.921(62)
$3^+_{30}-2^-_{20}$	632 901.712(27)
$3^+_{31}-2^-_{21}$	649 653.406(36)

[a]Observed frequencies corrected for the ion-drift Doppler shifts. Values in parentheses denote one standard deviation of the frequency measurements and apply to the last digits of the frequencies.

TABLE II. Molecular constants of the ground 0^+ and 0^- states of H_2DO^+ (MHz).

	Present study[a]	IR study[b]
$\nu(0^+-0^-)$	1 215 866 (410)[c]	1 214 700 (300)[d]
$A(0^+)$	331 735 (350)	333 171 (210)
$B(0^+)$	21 097 3(71)	210 970.2(51)
$C(0^+)$	140 265 (220)	140 031.8(36)
$\Delta_J(0^+)$	8.54[e]	
$\Delta_{JK}(0^+)$	53.9(74)	
$\Delta_K(0^+)$	−43.1(60)	473.4(51)
$A(0^-)$	326 638 (630)	32 318 5(63)
$B(0^-)$	20 896 0(97)	210 469 (120)
$C(0^-)$	141 422 (105)	14 068 7(57)
$\Delta_J(0^-)$	7.57[e]	
$\Delta_{JK}(0^-)$	47.78[f]	
$\Delta_K(0^-)$	−38.22[f]	

[a]Values in parentheses denote estimated errors and apply to the last digits of the constants, see the text. The δ_J and δ_K constants of the ground (0^+) and (0^-) states are fixed at 0.0.
[b]Reference 45.
[c]40.5569(137) cm^{-1}.
[d]40.518(10) cm^{-1}.
[e]Fixed at experimental values for D_3O^+ in Ref. 36. See the text.
[f]Fixed at the $\Delta_J(0^-)/\Delta_J(0^+)$ ratio.

The molecular constants of H_2DO^+ determined in the present study are compared in Table II with those by the high-resolution IR study.[45] The estimated uncertainties of the present molecular constants are slightly larger than those by the IR study. The $B_0(0^+)$ and $C_0(0^+)$ rotational constants of the present study agree within the quoted uncertainties with the corresponding constants by the IR study, but the $A_0(0^+)$ and all three rotational constants of the 0^- state significantly differ, both out of quoted uncertainties, from those by the IR study. As noted above, H_2DO^+ has a plane of symmetry, and two hydrogen atoms symmetrically located out of the symmetry plane only contribute to a difference between moments of inertia, $I_b-I_a-I_c$, which corresponds to $-I_c$ of H_3O^+. The difference, $I_b-I_a-I_c$, is calculated to be −2.7310(59) amu Å^2 for the 0^+ state and −2.7022(35) amu Å^2 for the 0^- state from

Table II, which can be compared with −2.7430 and −2.7067 amu Å^2 for $-I_c$ of H_3O^+,[34] respectively. A good agreement between the derived values for H_2DO^+ and H_3O^+ reflects a reliability of the rotational constants obtained in the present study, though inversion-rotation interaction may contribute to the moments of inertia of H_2DO^+ and H_3O^+ in a different way. On the other hand, the inertia difference from the IR result is calculated to be −2.730 41(97) amu Å^2 for the 0^+ state and −2.7548(20) amu Å^2 for the 0^- state. This suggests that only the rotational constants of the 0^+ state obtained in the IR study are also reliable.

The determined inversion splitting of 40.5569(137) cm^{-1} shows a very good agreement with 40.55(2) cm^{-1}, the predicted value discussed in the previous section and differs by 0.039 cm^{-1} from 40.518(10) cm^{-1} of the high-resolution IR spectroscopic study[45] and by −0.58 cm^{-1} from 41.14 cm^{-1} of the high-level quantum chemical calculation.[43] The precisely determined inversion splittings of H_3O^+ (Ref. 34) and D_3O^+ (Ref. 36) as well as H_2DO^+ will be a new challenging target for sophisticated high-level *ab initio* calculations. Dong and Nesbitt[45] carried out a calculation of the vibrational adiabatic one-dimensional model and derived the inversion barrier height and tunneling splittings in the vibrationally excited states for four isotopic species of H_3O^+. They compared the calculated results with the observed values and the predicted values by the high-level quantum mechanical calculations[43] and concluded that remaining small differences might be due to higher-order corrections beyond the Born-Oppenheimer approximation. Furthermore, so as to estimate the barrier height without an assumption of vibrational adiabaticity, they subjected the remaining differences to a semiclassical WKB tunneling analysis using the observed tunneling splittings and derived the barrier height of 653.0(7) cm^{-1} with one standard error in parentheses. As given above, we predicted the ground state inversion splitting of H_2DO^+ by using the empirical expression and the calculated inversion splittings of four deuterated species by the *ab initio* method. The analysis enabled us to correct the inversion splitting of H_2DO^+ in an accuracy of a few hundredth wave numbers. A reliable potential surface calculated by the high-level *ab initio* method,[43] though small shifts less than 1 cm^{-1} in energy remain, is essential for the present prediction. This practical method is very helpful for line-search experiments, because one-tenth order uncertainty in the tunneling splitting gives several gigahertz ambiguity in line frequency prediction.

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