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# Radiative cooling of H<sub>3</sub>O<sup>+</sup> and its deuterated isotopologues<sup>†</sup>

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In conjunction with *ab initio* potential energy and dipole moment surfaces for the electronic ground state, we have made a theoretical study of the radiative lifetimes for the hydronium ion  $H_3O^+$  and its deuterated isotopologues. We compute the ro-vibrational energy levels and their associated wavefunctions together with Einstein coefficients for electric dipole transitions. A detailed analysis of the stability of the ro-vibrational states has been carried out and the longest-living states of the hydronium ions have been identified. We report estimated radiative lifetimes and cooling functions for temperatures <200 K. A number of long-living meta-stable states are identified, capable of population trapping.

## 1 Introduction

In the Universe, molecules are found in a wide variety of environments: from diffuse interstellar clouds at very low temperatures to the atmospheres of planets, brown dwarfs and cool stars which are significantly hotter. In order to describe the evolution of the diverse, complex environments, it is essential to have realistic predictions of the radiative and cooling properties of the constituent molecules. Such predictions, in turn, require reasonable models for the energetics of each molecular species present.

Although interstellar molecular clouds are usually characterised as cold, they are mostly not fully thermalized. Whether a species attains thermal equilibrium with the environment depends on the radiative lifetimes of its states and the rate of collisional excitations to the states: this is normally characterised by the critical density. In non-thermalized regions, radiative lifetimes are also important for modelling the maser activity observed for many species. The long lifetimes associated with certain excited states can lead to population trapping and non-thermal, inverted distributions. Such unexpected state distributions have been observed for the  $H_3^+$  molecule both in space<sup>1,2</sup> and in the laboratory.<sup>3,4</sup>

Dissociative recombination of hydronium  $H_3O^+$  has been extensively studied in ion storage rings.<sup>5–9</sup> The lifetimes calculated in the present work suggest that  $H_3O^+$  and its isotopologues will exhibit population trapping in a manner similar to that observed for  $H_3^+$  in storage rings. Dissociative recombination of hydronium has been postulated as a possible cause of emissions from super-excited water in cometary comae<sup>10</sup> and as the mechanism for a spontaneous infrared water laser.<sup>11</sup>

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Hydronium and its isotopologues play an important role in planetary and interstellar chemistry.<sup>7,12</sup> These molecular ions are found to exist abundantly in both diffuse and dense molecular clouds as well as in comae. Moreover,  $H_3O^+$  is a water indicator and can be used to estimate water abundances when direct detection is unfeasible.<sup>13</sup> Consequently, the ions have been the subject of numerous theoretical and experimental studies (see, for example, ref. 7, 8, 12–46 and references therein) mainly devoted to the spectroscopy and chemistry of the species.

Whereas the cooling function of the  $H_3^+$  ion has been extensively studied by Miller et al.,47-49 no information about the radiative and cooling properties of H<sub>3</sub>O<sup>+</sup> and its deuterated isotopologues has been available thus far. In the present work, we remedy this situation by determining theoretically the ro-vibrational states of the ions  $H_3O^+$ ,  $H_2DO^+$ ,  $HD_2O^+$ , and  $D_3O^+$ . We use ab initio potential energy (PES) and dipole moment surfaces (DMS) for the ground electronic states of  $H_3O^+$  from ref. 50 to compute for each of the four ions considered here, ro-vibrational energy levels, the accompanying wavefunctions, and Einstein coefficients for the relevant ro-vibrational (electric dipole) transitions by means of the nuclear-motion program TROVE.<sup>51</sup> Lifetimes of individual ro-vibrational states are calculated and analyzed together with the overall cooling rates. Recently, the same methodology was used to estimate the sensitivities of hydronium-ion transition frequencies to a possible time variation of the proton-to-electron mass ratio.50

We present a detailed analysis of the stability of the ro-vibrational states of the hydronium ions and identify the states with the longest lifetimes. This study is based on the methodology<sup>52</sup> developed very recently as part of the ExoMol project.<sup>53</sup>

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The ExoMol project aims at a comprehensive description of the spectroscopic properties of molecules important for atmospheres of exoplanets and cool stars. The molecular lifetimes and cooling functions determined for  $H_3O^+$  and its deuterated isotopologues in the present work are available in the new ExoMol data format.<sup>54</sup>

#### 2 Theory and computation

The ro-vibrational energy levels and wavefunctions of the ions under study were calculated variationally using the TROVE program<sup>51,55</sup> in a manner similar to the successful calculations previously carried out for several other XY<sub>3</sub> pyramidal molecules<sup>56–61</sup> including ammonia NH<sub>3</sub> (see ref. 62 and 63), which exhibits the same large-amplitude, 'umbrella-flipping' inversion motion as H<sub>3</sub>O<sup>+</sup>. The inversion barrier of H<sub>3</sub>O<sup>+</sup> is 650.9 cm<sup>-1</sup>,<sup>64</sup> which is lower than 1791 cm<sup>-1</sup> found for NH<sub>3</sub>.<sup>39</sup> As a result, H<sub>3</sub>O<sup>+</sup> inversion splitting of the ro-vibrational ground state, 55.35 cm<sup>-1</sup> (ref. 65), is significantly larger than 0.793 cm<sup>-1</sup> (ref. 39) of NH<sub>3</sub>.

We have used *ab initio* PES and DMS of  $H_3O^+$  (ref. 50), computed at the MRCI/aug-cc-pwCV5Z(5Z) and MRCI/aug-cc-pwCVQZ(QZ) levels of theory, respectively. Complete basis set (CBS) extrapolation was used to obtain the Born–Oppenheimer PES (see ref. 50 for details).

The basis set used in the variational computations of the rovibrational states is defined in ref. 51. In all calculations of the present work, the orders of kinetic and potential energy expansions were set to 6 and 8, respectively. We used Morse-type basis functions for the stretching modes and numerical basis functions (numerical solutions of the corresponding 1D problem obtained within the framework of the Numerov–Cooley scheme<sup>66</sup>) for the bending vibrations. The *ab initio* equilibrium structure of  $H_3O^+$  is characterized by an O–H bond length of 0.9758 Å and a H–O–H angle of 111.95°. The vibrational basis set is controlled by the polyad number defined by

$$P = 2(\nu_1 + \nu_2 + \nu_3) + \nu_4 + \nu_5 + \nu_6/2, \tag{1}$$

where  $v_1$ ,  $v_2$ ,  $v_3$  represent the quanta of the stretching motion,  $v_4$  and  $v_5$  are those of the asymmetric bending motion and  $v_6$ is that of the primitive basis set functions for the inversion. In the present work, the maximum polyad number  $P_{\text{max}}$  (where  $P < P_{\text{max}}$ ) was set to 28. The ro-vibrational basis sets used for  $H_3O^+$  and  $D_3O^+$  were symmetrized according to the  $\mathcal{D}_{3h}(M)$ molecular symmetry group,67 while the calculations for the asymmetric isotopologues H<sub>2</sub>DO<sup>+</sup> and HD<sub>2</sub>O<sup>+</sup> were done under the  $\mathscr{C}_{2v}(M)$  symmetry. The computational details of the basis set construction can be found in ref. 62 as well as the details of the calculations of the Einstein coefficients Aif. The latter were computed for all possible initial, *i*, and final, *f*, states lying less than 600 cm<sup>-1</sup> above the zero point energy with  $J \leq 7$ . According to our estimations, this should be sufficient to describe the populations of the ro-vibrational states at thermodynamic temperatures up to 200 K. In this work we concentrate on the low energy applications. Higher temperatures would

require higher rotational excitations J and therefore more involved calculations.

The lifetimes of the states were computed as<sup>52</sup>

$$\tau_i = \frac{1}{\sum\limits_f A_{if}},\tag{2}$$

where the summation is taken over all possible final states f with energies lower than that of the given initial state i. The Einstein coefficients (in units of s<sup>-1</sup>) are defined as follows:<sup>68</sup>

$$A_{if} = \frac{64\pi^4 \tilde{\nu}_{if}{}^3}{3h(2J_f+1)} \sum_{m_i,m_f} \sum_{A=X,Y,Z} \left| \left\langle \Psi^{\rm f} | \bar{\mu}_A | \Psi^{\rm i} \right\rangle \right|^2, \qquad (3)$$

where *h* is Planck's constant,  $\tilde{\nu}_{if}$  (cm<sup>-1</sup>) is the wavenumber of the line,  $(hc\tilde{\nu}_{if}=E_f-E_i)$ ,  $J_f$  is the rotational quantum number for the final state,  $\Psi^i$  and  $\Psi^f$  represent the ro-vibrational eigenfunctions of the final and initial states, respectively,  $m_i$  and  $m_f$  are the corresponding projections of the total angular momentum on the *Z* axis, and  $\bar{\mu}_A$  is the electronically averaged component of the dipole moment (Debye) along the space-fixed axis A = X, Y, Z (see also ref. 69).

The cooling function W(T) is the total power per unit solid angle emitted by a molecule at temperature *T*; it is given by the following expression:<sup>52</sup>

$$W(T) = \frac{1}{4\pi Q(T)} \sum_{i,f} A_{if} h c \tilde{\nu}_{if} (2J_i + 1) g_i \exp\left(-\frac{c_2 \tilde{E}_i}{T}\right), \quad (4)$$

where  $g_i$  is the nuclear spin statistical weight factor of the state *i*. In the Boltzmann factor  $\exp(-c_2\tilde{E}_i/T)$ ,  $\tilde{E}_i (=E_i/hc)$  is the term

State	Sym.	Exp.	Ref.	Calc.	ExpCalc.
$H_3O^+$					
$\nu_2^+$	$A_1$	581.17	26	579.07	2.10
$2\nu_{2}^{+}$	$A_1$	1475.84	25	1470.67	5.17
$\nu_1^{+}$	$A_1$	3445.01	65	3442.61	2.40
$\nu_{3}^{+}$	E	3536.04	65	3532.58	3.46
$\tilde{\nu_4}^+$	E	1625.95	27	1623.02	2.93
$0^{-}$	$A_1$	55.35	65	55.03	0.32
$\nu_2^-$	$A_1$	954.40	26	950.94	3.46
$\nu_1^-$	$A_1$	3491.17	65	3488.32	2.85
$\nu_3^{-}$	E	3574.29	65	3571.04	3.25
$\nu_4^-$	E	1693.87	27	1690.65	3.22
$D_3O^+$					
$\nu_2^{+}$	$A_1$	453.74	31	451.58	2.16
$\nu_{3}^{+}$	E	2629.65	31	2627.14	2.51
0_	$A_1$	15.36	71	15.38	-0.02
$\nu_2^-$	$A_1$	645.13	31	642.79	2.34
$\nu_3^{-}$	E	2639.59	31	2637.10	2.49
$H_2DO^+$					
$0^{-1}$	$B_1$	40.56	43	40.39	0.17
$\nu_1^+$	$A_1$	3475.97	42	3473.27	2.70
$\nu_1^-$	$B_1$	3508.63	42	3505.51	3.12
$\nu_{3}^{+}$	$B_2$	3531.50	42	3528.07	3.43
$\nu_{3}^{-}$	$A_2^2$	3556.94	42	3553.63	3.31
$HD_{2}O^{+}$					
$0^{-}$	$B_1$	26.98	43	26.92	0.06

value of state *i* and  $c_2 = hc/k$  is the second radiation constant (*k* is the Boltzmann constant). The partition function Q(T) is defined as

$$Q(T) = \sum_{i} g_i (2J_i + 1) \exp\left(-\frac{c_2 \tilde{E}_i}{T}\right).$$
 (5)

Partition functions were computed for each ion employing the sets of ro-vibrational energies obtained with the chosen basis set.

The same PES and DMS were used for each isotopologue, which means that no allowance was made for the breakdown of the Born–Oppenheimer approximation. The energies of  $H_3O^+$  and the three deuterated isotopologues are very different not only due to the mass changes, but also due to the different symmetries these species belong to and the ensuing nuclear spin statistics. We use the molecular symmetry group<sup>67</sup>  $\mathcal{D}_{3h}(M)$  to classify the ro-vibrational states of the highest-symmetry species  $H_3O^+$  and  $D_3O^+$ , and  $\mathcal{C}_{2v}(M)$  for the lower-symmetry isotopologues  $H_2DO^+$  and  $HD_2O^+$ . The differences in the Einstein coefficients are also quite substantial, especially between the  $\mathcal{D}_{3h}(M)$  and the  $\mathcal{C}_{2v}(M)$  isotopologues. In general, isotope substitution in ions often leads to large changes in ro-vibrational intensities. This is because these intensities depend on the components of the

electric dipole moment in the molecule-fixed axis system which, by definition, has its origin in the nuclear center-of-mass. Upon isotopic substitution, the center-of-mass, and thus the origin of the molecule-fixed axis system, are displaced. For a neutral molecule (*i.e.*, a molecule with no net charge) this does not change the dipole moment components but, for an ion, they do (see, for example, ref. 70). Owing to intensities and Einstein coefficients changing much upon isotopic substitution, the lifetimes of the ro-vibrational states are expected to vary strongly with isotopologue for  $H_3O^+$ . Selection rules for *J* are

$$J' - J'' = 0, \pm 1 \text{ and } J' + J'' > 0.$$
 (6)

The symmetry selection rules for  $H_3O^{\scriptscriptstyle +}$  and  $D_3O^{\scriptscriptstyle +}$  are

$$A_1' \leftrightarrow A_1'', \quad A_2' \leftrightarrow A_2'', \quad E' \leftrightarrow E''$$
 (7)

where, for  $H_3O^+$  levels of  $A_1'$  and  $A_1''$  symmetry are missing<sup>67</sup> so that the associated selection rule is irrelevant, while those for  $H_2DO^+$  and  $HD_2O^+$  are

$$A_1 \leftrightarrow A_2, \quad B_1 \leftrightarrow B_2.$$
 (8)

Nuclear spin statistics<sup>67</sup> result in three distinct spin species of  $D_3O^+$ , *ortho* (ro-vibrational symmetry  $A_1'$  or  $A_1''$ , nuclear spin



Fig. 1 Calculated lifetimes  $\tau$  of the ro-vibrational states ( $J \le 7$ ) of H<sub>3</sub>O<sup>+</sup> and its deuterated isotopologues. The lifetime values are plotted logarithmically.

statistical weight factor  $g_{ns} = 10$ ), meta (E' or E'',  $g_{ns} = 8$ ) and para ( $A_2'$  or  $A_2''$ ,  $g_{ns} = 1$ ). As mentioned above,  $A_1'$  and  $A_1''$ ro-vibrational states are missing for  $H_3O^+$  and there are only ortho ( $A_2'$  or  $A_2''$ ,  $g_{ns} = 4$ ) and para (E' or E'',  $g_{ns} = 2$ ) states. The  $\mathcal{C}_{2v}(M)$ isotopologues  $H_2DO^+$  and  $HD_2O^+$  have ortho and para states: for  $H_2DO^+$ ,  $B_1$  and  $B_2$  states are ortho with  $g_{ns} = 9$ , and  $A_1$  and  $A_2$  states are para with  $g_{ns} = 3$ . For  $HD_2O^+$ , the ortho-para states are interchanged relative to  $H_2DO^+$ :  $A_1$  and  $A_2$  states are now ortho with  $g_{ns} = 12$  whereas  $B_1$  and  $B_2$  states are para with  $g_{ns} = 6$ .

#### 3 Results and discussion

In order to validate our description of the energetics of  $H_3O^+$ and its deuterated isotopologues, we compare in Table 1 calculated vibrational energies for these molecules with the available, experimentally derived values. In view of the fact that the calculations are based on a purely *ab initio* PES, the agreement between theory and experiment is excellent. The results suggest that the *ab initio* data used in the present work, in conjunction with the variational TROVE solution of the ro-vibrational Schrödinger equation, are more than adequate for obtaining accurate lifetimes of the molecules studied.

In Fig. 1, we plot the lifetimes calculated for the ro-vibrational states of  $H_3O^+$  and its deuterated isotopologues against the associated term values  $\tilde{E}$  ( $J \le 7$ ,  $\tilde{E} < 600 \text{ cm}^{-1}$ ). In general, the lifetimes exhibit the expected gradual decrease with increasing term value. The complete list of lifetimes for all four isotopologues is given as ESI<sup>†</sup> to this paper.

Lifetimes  $\tau$  of the longest-lived states of the ions are compiled in Table 2. The lowest-lying state of each of the nuclear spin species *ortho* and *para* (and *meta* for  $D_3O^+$ ) has an infinitely long lifetime; it has no state to decay to.

Low-lying, purely rotational states with low *J* values have the longest lifetimes; they have the smallest numbers of decay channels and/or the lowest probability for spontaneous emission transitions. The higher-symmetry species  $H_3O^+$  and  $D_3O^+$  (with  $\mathcal{D}_{3h}(M)$  symmetry) have more restrictive selection rules than the  $\mathcal{C}_{2v}(M)$  species  $HD_2O^+$  and  $H_2DO^+$ , and so  $H_3O^+$ and  $D_3O^+$  states live significantly longer (typically tens to hundreds of years) compared to the day-long lifetimes of  $HD_2O^+$  and  $H_2DO^+$ . Thus,  $D_3O^+$  has three meta-stable states with lifetimes longer than 100 years. The longest-lived of these, with  $\tau = 3816$  years, is the rotational state (J = 5, K = 5, E'') of the vibrational ground state. In comparison, the longest-lived meta-stable state of  $H_2DO^+$  the rotational state ( $J_{K_a,K_c},\Gamma$ ) = ( $1_{1,0},B_2$ ) has a lifetime of 265 days.

As mentioned above, the symmetry lowering from  $\mathcal{D}_{3h}(M)$  to  $\mathcal{C}_{2v}(M)$  gives rise to another important effect illustrated in Fig. 2. For  $H_3O^+$  and  $D_3O^+$  both the nuclear center-of-mass and the nuclear center-of-charge lie on the  $C_3$  symmetry axis for nuclear geometries with  $\mathcal{C}_{3v}$  geometrical symmetry.<sup>67</sup> We take the  $C_3$  axis to be the *z* axis of the molecule-fixed axis system whose origin, by definition, is at the nuclear center-of-mass. Consequently, at  $\mathcal{C}_{3v}$ -symmetry geometries the dipole moment lies along the *z* axis and its *x*- and *y*-components vanish.

The non-zero z-component is responsible for the parallel bands in the spectra of these species, including the rotation-inversion band<sup>44</sup> (the pure rotation band is forbidden by symmetry). Botschwina et al.<sup>18</sup> estimated the corresponding transition dipole for the inversion  $0^- \leftrightarrow 0^+$  band to be 1.47 D. Our *ab initio* value is slightly higher, 1.80 D. For  $H_2DO^+$  and  $HD_2O^+$ , the center-ofcharge obviously is unchanged relative to  $H_3O^+$  and  $D_3O^+$  but the center-of-mass is shifted, and this produces a non-vanishing perpendicular dipole moment at  $\mathscr{C}_{3v}$ -symmetry geometries. If we take the x axis to be in the plane defined by the  $C_3$  symmetry  $axis^{67}$  and the O-H bond for  $HD_2O^+$ , and in the plane defined by the  $C_3$  symmetry axis and the O–D bond for  $H_2DO^+$ , then  $HD_2O^+$ and  $H_2DO^+$  acquire non-vanishing x dipole moment components. Therefore the perpendicular transitions ( $\Delta K_c = \pm 1$ ) of H<sub>2</sub>DO<sup>+</sup> and  $HD_2O^+$  in the vibrational ground state are much stronger than the  $\Delta K = \pm 1$  transitions of  $H_3O^+$  and  $D_3O^+$  which are caused by intensity stealing from the vibrational spectrum.<sup>67</sup> Besides, this x component is larger for HD<sub>2</sub>O<sup>+</sup> than for H<sub>2</sub>DO<sup>+</sup> owing to the greater displacement of the nuclear center-of-mass. This is probably why the  $HD_2O^+$  lifetimes are shorter on the average than those of  $H_2DO^+$ . The z dipole moment component also changes with isotopic substitutions, see Fig. 2.

**Table 2** Lifetimes  $\tau$  for the longest-lived states of the H<sub>3</sub>O<sup>+</sup>, D<sub>3</sub>O<sup>+</sup>, H<sub>2</sub>DO<sup>+</sup>, and HD<sub>2</sub>O<sup>+</sup> ions. All states listed are rotational states in the vibrational ground state (*i.e.*, the inversion state 0<sup>+</sup>). The states are labeled  $(J, K, \Gamma)$  and  $(J_{K_a, K_c}, \Gamma)$  for  $\mathcal{D}_{3h}(M)$  and  $\mathscr{C}_{2v}(M)$  isotopologues, respectively, with  $\Gamma$  as the symmetry of the state in the respective group

State	Term value, $cm^{-1}$	τ
$\overline{H_3O^+}$		(Years)
$(1,0,A_2')$	22.47	)
(1,1,E'')	17.38	$\infty$
$(3,3,A_2'')$	88.96	$\infty$
(5,5,E'')	209.58	140.1
(2,1,E'')	62.29	26.2
(2,2,E')	47.03	23.9
(4,4,E')	143.15	17.7
$D_3O^+$		(Years)
$(0,0,A_1')$	0.00	<sup>oo</sup>
$(1,0,A_2')$	11.33	$\infty$
(1,1,E'')	8.78	$\infty$
$(3,3,A_2'')$	45.02	$\infty$
(5,5,E'')	106.15	3816.0
(2,2,E')	23.79	857.1
(4,4,E')	72.48	594.4
$(3,3,A_1'')$	45.02	190.4
$H_2DO^+$		(Days)
$(0_{0,0},A_1)$	0.00	x
$(1_{1,1},B_1)$	15.70	$\infty$
$(1_{1,0},B_2)$	18.07	265.4
$(2_{2,1},A_2)$	55.82	89.1
$(2_{2,0},A_1)$	56.60	4.8
$(1_{0,1},A_2)$	11.69	3
$HD_2O^+$		(Days)
$(0_{0,0},A_1)$	0.00	× ×
$(1_{1,1},B_1)$	9.53	$\infty$
$(1_{1,0},B_2)$	14.24	21.6
$(2_{2,1},A_2)$	35.35	8.9
$(1_{0,1},A_2)$	12.19	1.8
$(2_{2,0},A_1)$	27.77	1.4



Fig. 2 Displacements of the center-of-mass (green crosses) upon deuteration of  $H_3O^+$ . Arrows indicate the dipole moment components.

The longest-living states of  $D_3O^+$  (Table 2) have lifetimes about 27 times longer than those of  $H_3O^+$ . Presumably, this is mainly caused by the fact that  $D_3O^+$  has lower ro-vibrational term values than  $H_3O^+$ . Thus,  $D_3O^+$  has lower values of  $\tilde{\nu}_{if}$  in eqn (3) and this, in turn, causes lower Einstein-A coefficients and higher values of  $\tau$  [eqn (2) and (3)].

The calculated radiative cooling functions W(T) [eqn (4)] for  $H_3O^+$  and its deuterated isotopologues are shown in Fig. 3. At temperatures above 30 K the cooling decreases with increasing numbers of deuterium atoms in the molecule. This can be easily understood from eqn (3) and (4): W(T) is proportional to  $\tilde{\nu}_{ij}^{4}$ , and  $\tilde{\nu}_{ij}$  is approximately inversely proportional to the mass of hydrogen for the rotational states populated at the



Fig. 3 Calculated cooling functions of H<sub>3</sub>O<sup>+</sup> and isotopologues.

temperatures considered. Therefore, at moderate and high temperatures the lighter isotopologues are better coolers. However, Fig. 3 shows that at lower temperatures their roles change and the deuterated species become the better coolers. This is because the term values of the lowest, infinite-lifetime (and therefore coldest) states vary as 47.03 cm<sup>-1</sup> (2,2,*E*',0<sup>+</sup>), 23.79 cm<sup>-1</sup> (2,2,*E*',0<sup>+</sup>), 12.19 cm<sup>-1</sup> (1<sub>0,1</sub><sup>+</sup>,*A*<sub>2</sub>), and 11.69 cm<sup>-1</sup> (1<sub>0,1</sub><sup>+</sup>,*A*<sub>2</sub>) for H<sub>3</sub>O<sup>+</sup>, D<sub>3</sub>O<sup>+</sup>, HD<sub>2</sub>O<sup>+</sup>, and H<sub>2</sub>DO<sup>+</sup>, respectively. At very low temperatures, the molecules will tend to collect in the lowest accessible state, and the higher the term value of this state, the more difficult it is to cool the isotopologue in question. Because of this, for example, it is more difficult to cool H<sub>3</sub>O<sup>+</sup> than D<sub>3</sub>O<sup>+</sup> at temperatures below 30 K.

#### 4 Conclusions

We have carried out a theoretical study of the ro-vibrational states of the hydronium ion  $H_3O^+$  and its deuterated isotopologues. *Ab initio* potential energy and electric dipole moment surfaces were used to calculate ro-vibrational energy levels, corresponding wavefunctions and Einstein coefficients for the low-lying ro-vibrational transitions of these ions. We have analyzed the stability of the ro-vibrational states and computed the radiative lifetimes and cooling functions for temperatures below 200 K.

Taking into account only spontaneous emission as a cause of decay of ro-vibrational states (and neglecting collisions and stimulated emission) we find the longest-lived hydronium state for  $D_3O^+$ : the population in the rotational state with  $(J,K,\Gamma) = (5,5,E'')$  is trapped for 3816.0 years, which is relatively 'hot' (152 K), at least in the context of molecular cooling, for example in storage rings. In this work we have identified a number of relatively hot (E/k > 100 K) meta-stable states with a lifetime longer than 10 s (typical timescales of ion storage experiments). Such meta-stable states which will be populated and hamper the cooling of hydronium ions to a temperature of a few Kelvin. The molecule with the shortest-lived meta-stable states is  $HD_2O^+$  with lifetimes of a few days. The timescale of interstellar collisions in diffuse clouds is longer (about a month), and thus some of these states undergo spontaneous emission.

Our calculations show that deuteration influences significantly the hydronium lifetimes. This effect is mostly caused by the symmetry lowering from  $\mathcal{D}_{3h}(M)$  to  $\mathcal{C}_{2v}(M)$  and the ensuing perpendicular dipole moment component. A number of longliving meta-stable states are identified, capable of population trapping. Compared to the deuterated species, the cooling of the lightest isotopologue  $H_3O^+$  is most efficient at higher temperatures (T > 30 K). However, this changes at very low temperatures where the  $H_3O^+$  ions are trapped at relatively high energy.

The results obtained can be used to assess the cooling properties of the hydronium ion in ion storage rings and elsewhere.

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