Inversion-rotational spectrum of H_3O^+

M. G. Kozlov
Petersburg Nuclear Physics Institute, Gatchina 188300, Russia

(Dated: July 21 2010 – August 7, 2010)

The molecule H_3O^+ has inversion barrier significantly lower than that of NH_3. Consequently, the tunneling transition has higher frequency and mixes with rotational transitions. Several such FIR lines are observed from interstellar medium and these lines have *high* and *different* sensitivity coefficients to variation of electron-to-proton mass ratio μ.

PACS numbers: 06.20.Jr, 06.30.Ft, 33.20.Tp

I. SENSITIVITY COEFFICIENT OF INVERSION TRANSITION

The molecule H_3O^+ is similar to ammonia. It also has inversion barrier and tunneling transition. The hight of the barrier is much lower and the WKB approximation may be not applicable here. We still use it to get first estimate of the sensitivity. Following [1] we write for the inversion frequency (atomic units are used, where $\hbar = |e| = m_e = 1$):

$$\omega_{\rm inv} \approx \frac{2E_0}{\pi} {\rm e}^{-S}, \tag{1}$$

where S is the action over the classically forbidden region and E_0 is the ground state vibrational energy (note, that for anharmonic potential vibrational frequency $\omega_v \neq 2E_0$). Expression (1) gives following sensitivity to variation of electron-to-proton mass ratio μ [2]:

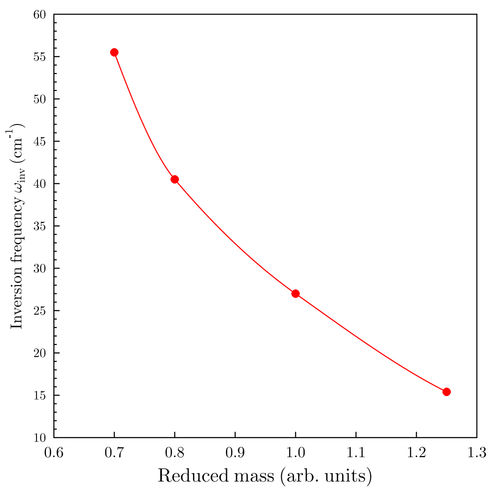
$$Q_{\rm inv} \approx \frac{S+1}{2} + \frac{S\,E_0}{2(U_{\rm max} - E_0)}\,, \tag{2}$$

where $U_{\rm max}$ is the barrier hight.

According to [3] we can take $U_{\rm max} = 651$ cm^{-1}. Figure 6 in [4] shows that $E_0 \approx 400$ cm^{-1}. Inversion frequency for H_3O^+ is 55 cm^{-1}, so Eqs. (1,2) give:

$$S \approx 1.5\,, \qquad Q_{\rm inv} \approx 2.5\,. \tag{3}$$

FIG. 1: Inversion frequency as a function of the reduced mass for hydronium ion isotopologues.



Ref. [4] reports inversion frequencies for H_3O^+, H_2DO^+, HD_2O^+, and D_3O^+ to be 55.3 cm^{-1}, 40.5 cm^{-1}, 27.0 cm^{-1}, and 15.4 cm^{-1} respectively. We can estimate reduced mass for the inversion mode of these molecules to scale

TABLE I: Frequencies and sensitivities to μ-variation of the inversion-rotation transitions in H_3O^+. Experimental frequencies are taken from Refs. [5, 7]

Transition						Frequency (MHz)		Q_μ	
J	K	s	J'	K'	s'	Exper.	Eq. (5)	Eq. (3)	Eq. (4)
1	0	−1	2	0	+1		298894	+9.2	+11.4
1	1	−1	2	1	+1	307192.410	307072	+9.0	+11.1
3	2	+1	2	2	−1	364797.427	365046	−5.7	−7.5
3	1	+1	2	1	−1	388458.641	389160	−5.2	−6.8
3	0	+1	2	0	−1	396272.412	397198	−5.1	−6.6
0	0	−1	1	0	+1	984711.907	984690	+3.5	+4.2
4	3	−1	3	3	+1	1031293.738	1031664	−1.4	−2.0
4	2	−1	3	2	+1	1069826.632	1071154	−1.2	−1.8
3	2	−1	3	2	+1	1621738.993	1621326	+2.5	+2.9
2	1	−1	2	1	+1	1632090.98	1631880	+2.5	+2.9
1	1	−1	1	1	+1	1655833.910	1655832	+2.5	+2.9

as 0.7, 0.8, 1.0, and 1.25 (see Fig. 5 in Ref. [4]). Then we can plot inversion frequency as a function of the reduced mass (see Fig. 1). From this plot we can estimate sensitivity coefficient for H_3O^+ to be:

$$Q_{\rm inv} \approx 2.9\,, \tag{4}$$

which is in reasonable agreement with Eq. (3). We can conclude that inversion transition in H_3O^+ is almost two times less sensitive to μ-variation, than similar transition in NH_3, where $Q_{\rm inv} = 4.5$ [2].

II. SENSITIVITIES OF THE MIXED TRANSITIONS

The spectrum of rotational and inversion transitions of H_3O^+ is studied in [5]. For the lowest vibrational state we can write the simplified inversion-rotational Hamiltonian as:

$$\begin{aligned} H = {} & BJ(J+1) + (C-B)K^2 - D_J[J(J+1)]^2 \\ & - D_{JK}J(J+1)K^2 - D_K K^4 + \ldots \\ & + \frac{s}{2}\left\{W_0 + W_J J(J+1) + W_K K^2 + \ldots\right\} . \end{aligned} \tag{5}$$

Here we neglected higher terms of expansion in J and K; $s = \pm 1$ for symmetric and antisymmetric inversion state; total parity $p = (-1)^K s$. Numerical values can be found from [5] (MHz):

B	$C-B$	D_J	D_{JK}	D_K	W_0	W_J	W_K
334406	−148804	35	−70	41	−1659350	5988	−8458

Note that we write Hamiltonian (5) in such a way, that terms which determine inversion splitting are collected in the last line. Therefore, we have following relation with parameters used in [5]:

$$B = \left(B(0^+) + B(0^-)\right)/2\,, \quad W_J = B(0^+) - B(0^-)\,, \tag{6}$$

and similarly for $C-B$ and W_K. Parameters D_J, D_{JK}, and D_K are averaged over inversion states $s = \pm 1$.

In order to find sensitivity of the mixed transition to μ-variation we need to know how parameters of the Hamiltonian (5) depend on μ. It is clear that B, $C \sim \mu$, and D_J, D_{JK}, $D_K \sim \mu^2$. Parameter W_0 scales as $\mu^{Q_{\rm inv}}$. It is less clear, what is the scaling of parameters W_J and W_K. In Ref. [2] we estimated scaling of analogous parameters in NH_3 to be $\sim \mu^{Q_{\rm inv}+0.5}$. We will assume the same scaling for the present case.

For a rough estimate of sensitivities of mixed transitions it must be sufficient to account only for μ-dependence of the dominant parameters B, C, and W_0. Then we can say, that $Q_{\rm rot} = 1$ and $Q_{\rm inv}$ is given by Eqs. (3), or (4). This leads to the expression, used earlier for NH_2D in [6]:

$$\omega_{\rm mix} = \omega_{\rm rot} \pm \omega_{\rm inv} \tag{7}$$

$$Q_{\rm mix} = \frac{\omega_{\rm rot}}{\omega_{\rm mix}} Q_{\rm rot} \pm \frac{\omega_{\rm inv}}{\omega_{\rm mix}} Q_{\rm inv} \tag{8}$$

We use Hamiltonian (5) and expression (8) to calculate frequencies and sensitivities of mixed transitions. Results are summed in the Table I. Sensitivities Q_μ are calculated for both values of $Q_{\rm inv}$. We see that final results are very sensitive to this parameter. In the next approximation, we need to weight independently all terms with different scalings, as discussed above. However, this does not lead to any significant changes to sensitivities Q_μ in Table I.

III. CONCLUSIONS

We see that mixed inversion-rotation transitions in hydronium ion H_3O^+ have rather high sensitivities to μ-variation. Even more important that several low frequency lines have sensitivities of opposite sign. Some of these lines were observed for interstellar medium and, therefore, can be used to check results, recently obtained with ammonia method [8–10]. In principle, other isotopologues of hydronium ion must also have high sensitivity to μ-variation. As we saw above, sensitivities of the mixed transitions strongly depend on the frequency and are particularly large for low-frequency transitions, $\omega_{\rm mix} \ll \omega_{\rm rot}, \omega_{\rm inv}$. Therefore, it is necessary to look for the low-frequency mixed transitions in the spectra of (partly) deuterated hydronium ions H_2DO^+, HD_2O^+, and D_3O^+.

Acknowledgments

I am grateful to V. Kokoouline for bringing inversion spectra of H_3O^+ to my attention and to S. Levshakov for comments and references.

[1] L. D. Landau and E. M. Lifshitz, *Quantum mechanics* (Pergamon, Oxford, 1977), 3rd ed.
[2] V. V. Flambaum and M. G. Kozlov, Phys. Rev. Lett. **98**, 240801 (2007), arXiv: 0704.2301.
[3] T. Rajamäki, J. Noga, P. Valiron, and L. Halonen, Molecular Physics **102**, 2259 (2004).
[4] F. Dong and D. J. Nesbitt, J. Chem. Phys. **125**, 144311 (2006).
[5] S. Yu, B. J. Drouin, J. C. Pearson, and H. M. Pickett, Astrophysical Journal Supplement **180**, 119 (2009).
[6] M. G. Kozlov, A. V. Lapinov, and S. A. Levshakov, J. Phys. B **43**, 074003 (2010), arXiv: 0908.2983, URL http://stacks.iop.org/0953-4075/43/074003.
[7] P. Chen, E. A. Cohen, T. J. Crawford, B. J. Drouin, J. C. Pearson, and H. M. Pickett, *JPL Molecular Spectroscopy Catalog*, http://spec.jpl.nasa.gov/, URL http://spec.jpl.nasa.gov/.
[8] S. A. Levshakov, P. Molaro, and M. G. Kozlov (2008), arXiv: 0808.0583.
[9] P. Molaro, S. A. Levshakov, and M. G. Kozlov, Nuclear Physics B Proceedings Supplements **194**, 287 (2009), arXiv: 0907.1192.
[10] S. A. Levshakov, P. Molaro, A. V. Lapinov, D. Reimers, C. Henkel, and T. Sakai, Astron. Astrophys. **512**, A44+ (2010), 0911.3732.