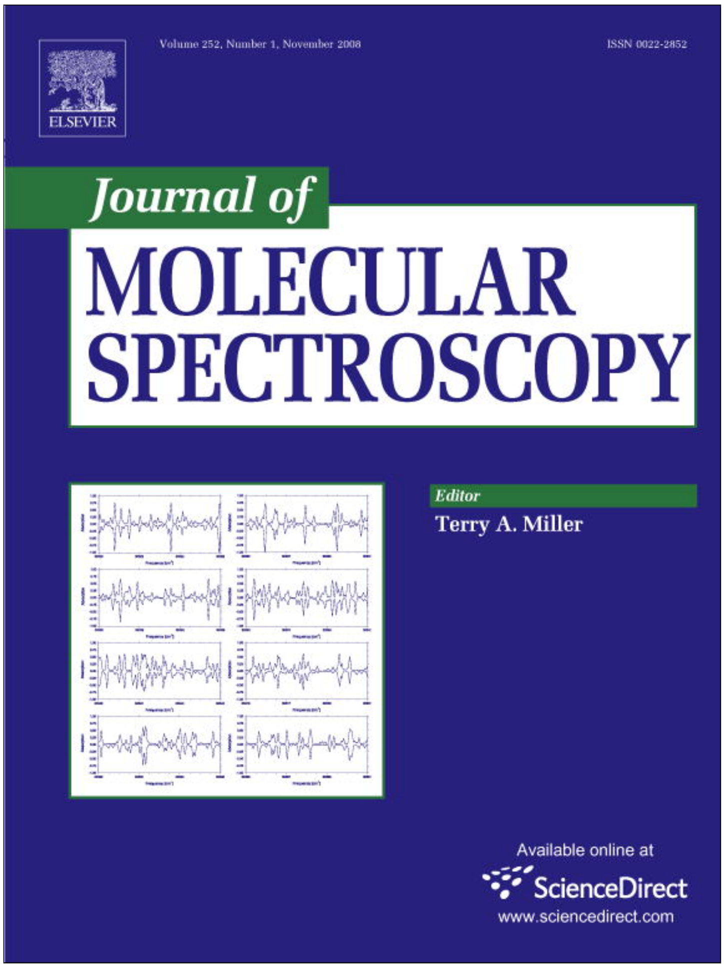
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Ab initio vibration–rotation spectra of triterated isotopologues of H_3^+

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ABSTRACT

Vibration–rotation energy levels for T_3^+, H_2T^+, T_2H^+, D_2T^+ and T_2D^+ are reported. These were calculated using the high accuracy model of Polyansky and Tennyson (J. Chem. Phys. 110 (1999) 5056) which explicitly allows for both adiabatic and non-adiabatic corrections to the Born–Oppenheimer approximation. These levels should be reliable to better than 0.05 cm^{-1} and can thus be used to make reliable predictions of infrared spectra for the triterated H_3^+ species.

1. Introduction

H_3^+ is the major molecular ion in cold hydrogen plasmas as it is rapidly formed from ionized molecular hydrogen via the reaction

$$H_2 + H_2^+ \rightarrow H_3^+ + H. \qquad (1)$$

It is expected therefore that plasmas containing T_2 will behave similarly and form triterated isotopologues of H_3^+.

There is renewed interest in the physics of molecules containing tritium for a number of reasons. For example ITER, the international project to design and build an experimental fusion reactor based on the tokamak concept, will burn tritium. Molecules are known to form at the plasma edge and in particular in the divertor region [1,2], understanding these regions is critical for the experiment. Similarly the KATRIN experiment [3,4] is being constructed to provide a laboratory measurement of the neutrino mass. This experiment uses T_2 and considerable effort has been made to understand the molecular physics of its decay to high accuracy [5,6]. As tritium undergoes β-decay, the tritium source will also be a weakly ionized leading to the formation of other species including potentially T_3^+ [7].

Tritium is not only radioactive but also very poisonous so laboratory studies of tritium containing compounds are very difficult and only performed under very special conditions. There are therefore no published spectra of triterated H_3^+ that we are aware of. Early theoretical studies on the spectroscopy of H_3^+ by Carney considered triterated species [8] however theoretical models have improved very considerably since then. In particular Polyansky and Tennyson [9,10] developed an *ab initio* model for H_3^+ spectra based on the ultra high accuracy electronic structure calculations of Cencek et al. [11]. This model made explicit allowance for both adiabatic and non-adiabatic corrections to the Born–Oppenheimer approximation. It was found to perform as well for deuterated isotopologues as it did for H_3^+ itself [9]. The accuracy of these calculations led Mielke et al. to describe this work as representing the third solved problem in molecular quantum mechanics [12]. There have been a number of more recent experimental studies [13–15] which have borne out the predictive accuracy of these calculations. Given this it would appear timely to apply the model of Polyansky and Tennyson, which is outlined in the following section, to the triterated isotopologues of H_3^+.

2. Calculations

All nuclear motion calculations were performed with the DVR3D program suite [16], which is based upon using exact kinetic energy operators within the context of the Born–Oppenheimer approximation. Given that it is well-established that this methodology is capable of giving results to spectroscopic accuracy [9,17], the accuracy of the model is dependent on the underlying potential energy surface and any allowance made for failure of the Born–Oppenheimer approximation.

As for previous studies of H_3^+ and its isotopologues [9,18,19], we write an effective potential energy surface, $W_i(R)$, as a function of internal coordinates, $\underline{Q}$, for the ith isotopologue as

$$W_i(\underline{Q}) = V_{BO}(\underline{Q}) + V_{rel}(\underline{Q}) + \frac{1}{\mu_i^S}\Delta V_{ad}^S(\underline{Q}) + \frac{1}{\mu_i^A}\Delta V_{ad}^A(\underline{Q}), \qquad (2)$$

where V_{BO} is the Born–Oppenheimer potential and V_{rel} is the electronic relativistic correction, both of which were taken from Cencek et al. [11].

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Table 1
Parameters, in atomic units, for the Morse oscillator-like functions [22] used to generate the radial grids in DVR3D [16]

	r_1			r_2		
	r_e	D_e	ω_e	r_e	D_e	ω_e
T_3^+	2.1	0.1	0.0118	1.71	0.26	0.009
H_2T^+	1.71	0.1	0.0108	1.65	0.215	0.00895
T_2H^+	1.83	0.09	0.0081	1.62	0.17	0.0105
D_2T^+	1.83	0.09	0.0081	1.62	0.17	0.0105
T_2D^+	1.83	0.09	0.0081	1.62	0.17	0.0105

The mass-dependent terms in (2) are due to the adiabatic correction to the BO approximation. For T_3^+ only the symmetric adiabatic correction, ΔV^S_{ad}, is non-zero. The mass factor for this term is

$$(\mu_i^S)^{-1} = m_A^{-1} + m_B^{-1} + m_C^{-1}. \tag{3}$$

For all other species considered here it is also necessary to include the asymmetric adiabatic correction, ΔV^A_{ad}, which has a mass factor

$$(\mu_i^A)^{-1} = m_A^{-1} - m_B^{-1}, \tag{4}$$

within a labeling scheme for which $m_B = m_C$ [18,19]. Nuclear masses were used for these mass factors. We note that this formulation does not allow for the case of HDT^+ where all three atoms are different. We do not treat HDT^+ in this work although doing so, which would require extending the treatment of the Born–Oppenheimer correction terms, should be reasonably straightforward.

As before non-adiabatic effects were modelled using effective vibrational masses [9]. The vibrational masses used were derived from the formula of Bunker and Moss [20] which gives $m_H = 1.0075372$ u, $m_D = 2.0138140$ u and $m_T = 3.01629259$ u. These can be compared to values for the nuclear mass of $m_H = 1.00727647$ u, $m_D = 2.0135532$ u and $m_T = 3.01604927$ u [21] which were used for the rotational masses. We note that the larger mass of tritium means that we would expect non-adiabatic effects to be reduced in the triterated isotopologues. This is reflected by the small ratio of the effective vibrational mass to the nuclear mass for tritium.

The nuclear motion calculations were all performed in Jacobi coordinates with the z-axis fixed along the atom–diatom coordinate. Discrete variable representation (DVR) grids based on Morse-oscillator-like functions [22] were used to represent the radial motions and DVR grids from Gauss-(associate) Legendre polynomials were used for the angular coordinate. Extensive convergence tests were performed and the basis sets chosen gave stable results to within 0.002 cm^{-1} for the energies quoted below.

Parameters for the Morse-oscillator-like functions are given in Table 1. The DVR3D calculations all used 21 grid points in r_2, 20 in r_1 and 36 in the angle θ, except for those on D_2T^+ where it was found necessary to use a larger r_2 grid with 28 points to obtain convergence. The final vibrational Hamiltonian was taken to be of dimension 2000 and the rotation–vibration one $350 \times (J + 1)$.

3. Results

At low temperatures the different zero point energies of the various isotopologues can give rise to pronounced fractionation effects. Such processes are known to be astrophysically important for deuteratation of H_3^+ [23]. Table 2 gives the energies of the $J = 0$ vibrational ground state for the triterated isotopologues considered here. Due to nuclear spin effects, see below, lowest allowed state for T_3^+ is for $J = 1$ which adds an extra 21.6 cm^{-1} to the zero point energy for this species. The equivalent data for deuterated isotopologues have calculated previously using the same model [24].

Table 2
Energy of the $J = 0$ vibrational ground state in cm^{-1} relative to the minimum of the potential energy surface for triterated isotopologues of H_3^+

T_3^+	2552.88
H_2T^+	3919.47
T_2H^+	3290.17
D_2T^+	2982.87
T_2D^+	2789.99

Since the spectroscopy of T_3^+ is rather different from the mixed isotopologues, which all possess a permanent dipole moment, they will be dealt with separately.

3.1. T_3^+

The tritium nucleus has spin half like the proton. This means that the vibration–rotation levels of T_3^+ obey the same rules as those of H_3^+ and in particular those of A_1 symmetry are missing. Furthermore the absence of a permanent dipole means that transitions pure rotational transitions are only very weakly allowed [25] and, indeed, have yet to be observed for H_3^+.

Table 3 gives energy levels for the low-lying rotation–vibration states of T_3^+. There are several conventions for labelling the rotation–vibration levels of H_3^+; we have used the standard vibrational state labels, (ν_1, ν_2^ℓ), and rotational labels (J,G). Here we follow the proposal of Lindsay and McCall [26] and use the subscripts u and l to further distinguish states where necessary; we refer the reader to this paper for a discussion of this issue. Table 3 omits the Pauli forbidden rotationally excited levels of T_3^+ but leaves the vibrational band origins even when they are of A_1 symmetry as this information can be useful. A fuller listing of T_3^+ rotation–vibration energy levels covering both rotational levels with J up to 5 and higher vibrational states is given in the Supplementary data. It should be noted that since our calculations were performed in Jacobi coordinates they do not automatically give the full symmetry of the T_3^+ system.

Table 3
Vibration–rotational energy levels in cm^{-1} for the vibrational fundamentals and first bending overtone of T_3^+

JG	ν_0	ν_1	$2\nu_2^0$
00		1899.656	2940.884
10	21.605	1920.930	2962.327
11	29.101	1928.322	2970.526
22	57.397	1956.163	2997.062
21	79.835	1978.293	3021.468
33	107.302	2005.284	3045.039
32	144.616	2042.086	3085.436
31	166.921	2064.086	3109.209
30	174.343	2071.404	3118.651
	ν_2^1	JG	$2\nu_2^2$
01	1517.843	02	3024.266
12	1526.045	13	3020.844
11	1547.089	12	3053.637
10	1553.594	11	3070.551
23	1548.076	24	3030.462
22	1584.588	23	3078.888
$(21)_l$	1600.058	22	3112.427
$(21)_u$	1606.607	21	3129.362
20	1608.103	20	3130.055
34	1583.865	35	3053.679
33	1635.800	34	3117.065
$(32)_l$	1661.896	33	3168.733
$(32)_u$	1673.539	$(31)_l$	3200.597
$(31)_u$	1684.990	32	3203.042
30	1696.570	30	3217.564
$(31)_l$	1704.313	$(31)_u$	3219.043

Table 4
Rotational energy levels in cm^{-1} for the vibrational ground states of the mixed isotopologues

JK_aK_c	H_2T^+	D_2T^+	T_2H^+	D_2T^+
101	39.158	26.230	24.445	22.650
111	58.263	31.025	43.557	27.448
110	67.592	38.781	48.286	33.960
202	114.677	74.048	72.512	64.359
212	127.131	75.682	87.667	66.201
211	154.990	98.886	101.810	85.692
221	211.974	113.227	158.920	100.043
220	214.594	117.787	159.681	103.576
303	222.262	139.859	142.707	121.947
313	228.767	140.232	153.305	122.431
312	283.633	184.411	181.390	159.858
322	328.703	191.610	231.938	167.761
321	340.514	208.729	235.591	181.425
331	446.999	236.899	338.545	209.526
330	447.470	238.938	338.621	210.943
404	358.944	223.529	233.362	195.093
414	361.811	223.599	239.943	195.198
413	450.146	289.617	286.094	251.882
423	481.698	292.039	328.478	254.939
422	511.665	328.869	338.617	285.015
432	605.571	346.628	436.732	304.002
431	608.634	357.222	437.248	311.755
441	763.265	402.068	582.673	356.083
440	763.333	402.815	582.679	356.546
505	524.000	325.331	343.339	284.059
515	525.135	325.343	347.053	284.080
514	649.931	411.759	414.579	358.892
524	669.007	412.362	447.881	359.781
523	725.803	472.404	468.970	409.986
533	802.644	480.678	559.319	419.978
532	813.416	508.170	561.285	441.122
542	960.290	540.989	704.646	475.424
541	960.856	546.303	704.699	478.890
551	1158.256	608.352	889.720	539.485
550	1158.264	608.593	889.720	539.619

Table 5
Vibration–rotational energy levels in cm^{-1} for the vibrational fundamentals of the mixed isotopologues

JK_aK_c	ν_2	ν_3	ν_1
H_2T^+			
000	2046.141	2267.488	2953.355
101	2083.331	2306.583	2992.849
111	2100.818	2329.668	3009.505
110	2113.594	2336.548	3019.339
202	2152.881	2383.158	3068.477
212	2162.586	2400.589	3078.536
211	2200.509	2421.324	3107.903
221	2252.666	2490.063	3157.585
220	2257.465	2491.313	3160.757
303	2248.901	2483.299	3175.427
313	2253.037	2505.466	3180.137
312	2326.551	2547.008	3237.817
322	2364.049	2606.057	3275.305
321	2384.189	2612.128	3289.266
331	2494.437	2736.893	3383.072
330	2484.692	2737.021	3383.734
D_2T^+			
000	1699.050	1741.707	2201.157
101	1720.124	1772.573	2227.183
111	1723.656	1778.845	2231.488
110	1737.887	1780.885	2239.280
202	1755.281	1829.864	2274.355
212	1755.981	1833.985	2275.700
211	1794.136	1844.570	2299.017
221	1804.684	1863.285	2311.888
220	1816.089	1863.201	2316.692
303	1805.059	1908.220	2339.202
313	1805.173	1910.828	2339.479
312	1868.830	1935.931	2383.635
322	1872.171	1950.757	2389.655
321	1904.775	1955.535	2407.388
331	1926.815	1991.253	2432.724
330	1934.565	1990.804	2435.021
T_2H^+			
000	1650.723	1901.719	2619.302
101	1673.644	1927.283	2643.521
111	1694.370	1944.273	2662.268
110	1699.747	1949.459	2666.898
202	1718.562	1977.285	2691.155
212	1734.768	1990.264	2706.033
211	1750.809	2005.761	2719.876
221	1812.649	2005.761	2775.872
220	1813.506	2057.510	2776.614
303	1783.833	2049.884	2760.776
313	1794.926	2058.448	2771.205
312	1826.662	2089.139	2798.649
322	1880.845	2133.683	2848.256
321	1884.944	2138.356	2851.813
331	1996.385	2230.478	2952.659
330	1996.510	2230.600	2952.733
T_2D^+			
000	1596.427	1626.043	2074.351
101	1613.551	1655.883	2096.760
111	1617.588	1657.379	2101.340
110	1630.693	1660.013	2107.795
202	1643.511	1707.444	2137.953
212	1644.447	1712.422	2139.673
211	1677.262	1723.347	2158.989
221	1688.894	1727.403	2172.689
220	1696.209	1728.998	2176.255
303	1686.662	1775.218	2194.816
313	1686.842	1782.513	2195.258
312	1741.312	1806.225	2232.283
322	1745.711	1823.735	2239.706
321	1766.898	1828.639	2253.401
330	1793.929	1833.533	2280.239
331	1793.248	1834.296	2281.705

Since the transitions to ν_1 breathing fundamental are weak [27], the most promising transitions for observation are those in the degenerate ν_2 bending fundamental, although it should be noted that transitions to states of the $2\nu_2$ bending overtone should also be strong [28].

3.2. Mixed isotopologues

Table 4 gives the low-lying rotational levels of the asymmetric isotopologues H_2T^+, T_2H^+, D_2T^+ and T_2D^+. The corresponding levels for the vibrational fundamentals, the excitation of all of which should give rise to strong transitions, are given in Table 5. Again a much more complete set of energy levels are given in the Supplementary data. However these levels are only labelled by rigorous quantum numbers, not the conventional but approximate normal mode, (ν_1,ν_2,ν_3), asymmetric top, (J,K_a,K_c) quantum numbers used in the tables. It is well known from studies of H_2D^+ [29,30] that the labelling of the levels belonging to vibrationally excited states can be problematic. This arises particularly from the strong Coriolis interaction between the ν_2 and ν_3 vibrational states.

4. Conclusion

The *ab initio* model of Polyansky and Tennyson [9] has been applied to tritium containing isotopologues of H_3^+. This model has proved to be highly accurate for H_3^+ itself and deuterated isotopologues. The dominant residual errors in this model are thought to be due to a still incomplete treatment of corrections to the Born–Oppenheimer approximation [13]. Given that these corrections should be smaller for the heavier triterated species there is reason to believe that the predicted rotation–vibration energy levels presented here should be at least as accurate and probably more accurate than those calculated previously for the non-triterated isotopologues.

The present study gives only energy levels. Many practical applications will also require transition intensities. These are straightforward to calculate using wavefunctions generated as part of this work. Such predicted intensities have been shown to be reliable [15,31]. However it is hard to predict spectral regions and temperatures that will be need in actual applications. Such spectra can be generated on request; such requests should be addressed to the last author.

Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://library.osu.edu/sites/msa/jmsa_hp.htm). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jms.2008.06.008.

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