

# Zero point energy of $\text{H}_3^+$ and its deuterated isotopomers

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**Abstract.** Vibrational zero-point energies are reported for the  $\text{H}_3^+$ ,  $\text{H}_2\text{D}^+$ ,  $\text{D}_2\text{H}^+$  and  $\text{D}_3^+$  molecular ions, calculated using an ultra-high accuracy ab initio procedure. These data are compared with older literature values.

**Key words.** astrochemistry – molecular data – molecular processes, ISM: general – ISM molecules – ISM: kinematic and dynamics

## 1. Introduction

The simple molecular ion  $\text{H}_3^+$  is rapidly formed by the reaction



$\text{H}_3^+$  has long been identified as the main driver of gas phase, ion-molecule chemistry in the interstellar medium. Its spectrum has been observed in a number interstellar environments (Geballe 2000) suggesting that not only is  $\text{H}_3^+$  indeed present in dense molecular clouds at approximately the density predicted by most models, but also that there is more of it in diffuse clouds than had previously been anticipated (see McCall et al. 2002, for example). The interstellar emission spectrum of  $\text{H}_2\text{D}^+$  was observed by Stark et al. (1999) and, very recently, much more securely by Caselli et al. (2003).

Fractionation effects at low temperatures have long been expected (Dalgarno & Lepp 1984) to produce greatly enhanced relative abundances of  $\text{H}_2\text{D}^+$  in low temperature environments, primarily via the reaction:



This reaction is exothermic due to the effects of zero-point vibrational motion. Combining our calculations with zero point energies for  $\text{H}_2$  and  $\text{HD}$  taken from Huber & Herzberg (1979) gives a value of 231.8 K for the exothermicity. The temperature dependence of this reaction was the subject of a theoretical study by Sidhu et al. (1992).  $\text{H}_2\text{D}^+$  is known to play a major role in the deuteration of interstellar molecules (Millar et al. 2000).

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Recent observations have identified several multiply deuterated species in the interstellar medium (Loinard et al. 2001; Ceccarelli 2002). Species observed include doubly and triply deuterated ammonia (Tine et al. 2000):  $\text{NHD}_2$  (Roueff et al. 2000; Rodgers & Charnley 2001; Parise et al. 2002) and  $\text{ND}_3$  (van der Tak et al. 2002; Lis et al. 2002), doubly deuterated formaldehyde:  $\text{D}_2\text{CO}$  (Ceccarelli et al. 1998; Loinard et al. 2000; Ceccarelli et al. 2002), doubly deuterated methanol:  $\text{CHD}_2\text{OH}$  (Parise et al. 2002), and very recently doubly deuterated hydrogen sulphide:  $\text{D}_2\text{S}$  (Vastel et al. 2003).

In the gas phase, fractionation reactions are driven by differences in vibrational zero-point energies. Zero-point energies for  $\text{H}_3^+$  and its deuterated isotopomers,  $\text{H}_2\text{D}^+$ ,  $\text{D}_2\text{H}^+$  and  $\text{D}_3^+$ , were reported some time ago by Carney (1980), see also Jensen et al. (1986). However recent ab initio studies (Cencek et al. 1998; Polyansky & Tennyson 1999) mean that such values can be determined to much greater accuracy and it is these values that we report here.

## 2. Calculations

The calculations are based on those reported by Polyansky & Tennyson (1999) (PT), where further details can be found. In particular, PT employed the ultra-high accuracy ab initio potential energy and adiabatic correction surfaces of Cencek et al. (1998). PT fitted new surfaces to the ab initio data computed by Cencek et al. This point is probably not important here as far as the Born-Oppenheimer potential is concerned but PT's adiabatic or Born-Oppenheimer Diagonal Correction (BODC) surfaces differed significantly from those of Cencek et al. The BODC is important for modelling the difference in behaviour between isotopomers. In addition PT used the vibrational mass to model non-adiabatic effects. The results predict transition frequencies to within a few hundredths of a wavenumber ( $\text{cm}^{-1}$ ) and are therefore of very high accuracy (see also Kostin et al. 2002).

**Table 1.** Comparison of vibrational zero point energies for deuterated  $\text{H}_3^+$ .  $\Delta(zpe)$  is the change in zero point energy relative to the lowest  $J = 1, K = 1$  level of  $\text{H}_3^+$ .

Isotopomer	Zero point energy [ $\text{cm}^{-1}$ ]			$\Delta(zpe)$ [K]
	Carney (1980)	Jensen et al. (1986)	This work	This work
$\text{H}_3^+$	4345.3		4361.7	0.0
$\text{H}_2\text{D}^+$	3963.0	3993.3	3978.1	−644.2
$\text{D}_2\text{H}^+$	3547.5	3571.5	3561.4	−1243.8
$\text{D}_3^+$	3099.8		3112.3	−1890.0

Table 1 gives vibrational zero-point energies calculated for the four H/D isotopomers of  $\text{H}_3^+$ . These are compared to the values given by Carney (1980) and the semi-empirical values for the mixed isotopomers given by Jensen et al. (1986). For  $\text{H}_3^+$ , occupation of the rotational ground state of the system is forbidden by the Pauli principle. The lowest state has  $J = 1, K = 1$  and lies, according to our calculations, a further  $64.123 \text{ cm}^{-1}$  higher.

For astrophysical applications it is not the absolute zero-point energies themselves that are important but the change in these values,  $\Delta(zpe)$ , which matter. Our values for  $\Delta(zpe)$  should be reliable to 0.1 K since the calculations reproduce the observed experimental transition frequencies for  $\text{H}_3^+$  and its isotopomers to significantly better than this.

We note that our new results for  $\Delta(zpe)$  differ by several degrees from previous values. For example we calculate that  $\Delta(zpe)$  for  $\text{H}_2\text{D}^+$  relative to  $\text{H}_3^+$ , in its  $J = 1$  ground state, is 644.2 K which can be compared to 642 K given by Carney (1980) and the value 644 K employed by Sidhu et al. (1992). Similarly we obtain  $\Delta(zpe)$  for  $\text{H}_2\text{D}^+$  relative to  $\text{D}_2\text{H}^+$  of 599.6 K compared to 598 K from Carney (1980) and the more recent, but less accurate, value of 607 K from Jensen et al. (1986).

### 3. Conclusions

We have calculated accurate zero-point energies for the astrophysically important ion  $\text{H}_3^+$  and its isotopomers. Our absolute vibrational zero-point energies differ quite significantly from some previously reported values. Conversely the variations, between our calculations and previous studies, in energy differences caused by zero-point effects are somewhat smaller, only a few degrees. However we note that most fractionation reactions are only weakly exothermic and thus even small energy differences may be significant. We hope that these new, high accuracy data, will be of use for models of fractionation effects, particularly those involving multiply deuterated molecules.

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### References

- Carney, G. D. 1980, *Chem. Phys.*, 54, 103
- Caselli, P., van der Tak, F. F. S., Ceccarelli, C., & Bacmann, A. 2003, *A&A*, 403, L37
- Ceccarelli, C. 2002, *Planet Space Sci.*, 50, 1267
- Ceccarelli, C., Castets, A., Loinard, L., Caux, E., & Tielens, A. G. G. M. 1998, *A&A*, 338, 43
- Ceccarelli, C., Vastel, C., Tielens, A. G. G. M., et al. 2002, *A&A*, 381, 17
- Cencek, W., Rychlewski, J., Jaquet, R., & Kutzelnigg, W. 1998, *J. Chem. Phys.*, 108, 2831
- Dalgarno, A., & Lepp, S. 1984, *ApJ*, 287, L47
- Geballe, T. R. 2000, *Philos. Trans. R. Soc. Lond. Ser. A-Math. Phys. Eng. Sci.*, 358, 2503
- Huber, K. P., & Herzberg, G. 1979, *Constants of diatomic molecules* (New York: Van Nostrand)
- Jensen, P., Špirko, V., & Bunker, P. 1986, *J. Molec. Spectrosc.*, 115, 269
- Kostin, M. A., Polyansky, O. L., & Tennyson, J. 2002, *J. Chem. Phys.*, 116, 7564
- Lis, D. C., Roueff, E., Gerin, M., et al. 2002, *ApJ*, 571, 55
- Loinard, L., Castets, A., Ceccarelli, C., Caux, E., & Tielens, A. G. G. M. 2001, *ApJ*, 552, 163
- Loinard, L., Castets, A., Ceccarelli, C., et al. 2000, *A&A*, 359, 1169
- McCall, B. J., Hinkle, K. H., Geballe, T. R., et al. 2002, *ApJ*, 567, 391
- Millar, T. J., Roberts, H., Markwick, A. J., & Charnley, S. B. 2000, *Philos. Trans. R. Soc. Lond. Ser. A-Math. Phys. Eng. Sci.*, 358, 2535
- Parise, B., Ceccarelli, C., Tielens, A. G. G. M., et al. 2002, *A&A*, 393, L49
- Polyansky, O. L., & Tennyson, J. 1999, *J. Chem. Phys.*, 110, 5056
- Rodgers, S. D., & Charnley, S. B. 2001, *ApJ*, 553, 613
- Roueff, E., Tine, S., Coudert, L. H., et al. 2000, *A&A*, 354, 63
- Sidhu, K. S., Miller, S., & Tennyson, J. 1992, *A&A*, 255, 453
- Stark, R., van der Tak, F. F. S., & van Dishoeck, E. F. 1999, *ApJ*, 521, 67
- Tine, S., Roueff, E., Falgarone, E., Gerin, M., & Pineaux des Forets, G. 2000, *A&A*, 356, 1039
- van der Tak, F. F. S., Schilke, P., Muller, H. S. P., et al. 2002, *A&A*, 388, 53
- Vastel, C., Ceccarelli, C., et al. 2003, *A&A*, submitted