Monthly Notices
of the
ROYAL ASTRONOMICAL SOCIETY

Mon. Not. R. Astron. Soc. **402,** 492–496 (2010) doi:10.1111/j.1365-2966.2009.15904.x

A high accuracy computed line list for the HDO molecule

B. A. Voronin,[1] J. Tennyson,[2]★ R. N. Tolchenov,[2] A. A. Lugovskoy[1] and S. N. Yurchenko[3]

[1]*Zeuv Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, Tomsk 634021, Russia*
[2]*Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT*
[3]*Technische Universität Dresden, Institut für Physikalische Chemie und Elektrochemie, D-01062 Dresden, Germany*

Accepted 2009 October 16. Received 2009 October 14; in original form 2009 August 19

ABSTRACT

A computed list of $HD^{16}O$ infrared transition frequencies and intensities is presented. The list, VTT, was produced using a discrete variable representation two-step approach for solving the rotation–vibration nuclear motions. The VTT line list contains almost 700 million transitions and can be used to simulate spectra of mono-deuterated water over the entire temperature range that are of importance for astrophysics. The line list can be used for deuterium-rich environments, such as the atmosphere of Venus, and to construct a possible 'deuterium test' to distinguish brown dwarfs from planetary mass objects.

Key words: line: identification – molecular data – techniques: spectroscopic – astronomical data bases: miscellaneous – infrared: general.

1 INTRODUCTION

Water is the most abundant molecule in our Universe after H_2 and CO. It is present in its partially deuterated form and is well known in a number of astrophysical environments. Astrophysical observations of HDO are also potentially important. Deuterium was formed in the first few minutes after the big bang. As D is burnt rapidly in stellar interiors, the abundance of D has been decreasing since this time. Deuterium burns in objects with masses greater than about 13 times that of Jupiter, which has led to the suggestion of a 'deuterium test' (Bejar, Osorio & Rebolo 1999) defining the boundary between a brown dwarf and a planet. Observations of HDO or other absorption by deuterated molecules in the atmospheres of such objects, which are cool enough to be largely molecular but hot by terrestrial standards, could be the key to this test (Pavlenko et al. 2008).

In the cold interstellar medium, fractionation effects become important leading to an expected overabundance of HDO (Hewitt et al. 2005). HDO has been observed in Orion KL (Olofsson et al. 2007) and in the early stages of star formation (Stark et al. 2004). Observation of atmospheric HDO spectra has long been used on both the Earth (Joussaume, Sadourny & Jouzel 1984) and other planets (Fouchet & Lellouch 2000; Montmessin, Fouchet & Forget 2005) as a means to understand their climatic evolution. The increased relative abundance of deuterium on Venus leads to particularly strong HDO spectra (De Berg et al. 1991). HDO is also well known in cometary spectra (Bockelee-Morvan et al. 1998; Villanueva et al. 2009).

★E-mail: j.tennyson@ucl.ac.uk

HDO has been the subject of many room-temperature laboratory studies (see Voronin et al. 2007 and references therein). However, there are only two published studies of hot spectra: both emission spectra recorded by Bernath and co-workers (Parekunnel et al. 2001; Janca et al. 2003) which span frequencies up to 4000 cm^{-1}. HDO experimental data were the subject of a recent compilation (Tennyson et al. 2009b) by an International Union of Pure and Applied Chemistry (IUPAC) task group (Tennyson et al. 2009a) for which the line list reported here was used for validation purposes.

There are a number of calculated line lists for $H_2{}^{16}O$ (Allard et al. 1994; Partridge & Schwenke 1997; Viti, Tennyson & Polyansky 1997; Jorgensen et al. 2001; Barber et al. 2006). The present work can be thought of as a companion for the recent BT2 $H_2{}^{16}O$ line list of Barber et al. (2006) which has proved important for a variety of astronomical studies (Banerjee et al. 2005; Dello Russo et al. 2005; Tinetti et al. 2007; Viti et al. 2008; Bailey 2009; Barber et al. 2009). There is only one previously published line list for hot HDO which was due to Partridge & Schwenke (1997). For computational reasons, some of which are discussed below, this line list was both less extensive and less accurate than their widely used line list for H_2O. This situation has been improved by Tashkun (unpublished) who recomputed HDO line lists using the methodology of Partridge and Schwenke, although, as discussed elsewhere (Yurchenko et al. 2008), there remain problems even with these improved line lists.

Here, we present a significantly improved, in terms of both accuracy and coverage, line list for HDO. This line list, which we call VTT, forms part of our attempt to systematically generate line lists for key astronomical molecules (Tennyson et al. 2007). In the following section, we describe the theoretical techniques used in the calculation. Section 3 presents sample results for the line list,

which we make generally available electronically. The final section presents our conclusions.

2 CALCULATIONS

The accurate calculation of a rotation–vibration line list requires a number of components: a potential energy surface (PES) on which to perform the calculation, a dipole moment surface (DMS) to obtain the transition intensities, the necessary software to make the computation and significant computer resources. In addition, and in particular for hydrogen-containing species, allowance must be made for failure of the Born–Oppenheimer approximation. This is particularly true for HDO where the asymmetric substitution leads to changes in the vibrational structure which cannot be entirely accounted for within the Born–Oppenheimer framework (Zobov et al. 1996).

In this work, we use the HDO07 PES of Yurchenko et al. (2008). This surface is a refinement of the *ab initio* CVRQD surface (Polyansky et al. 2003; Barletta et al. 2006) specifically for HDO and therefore explicitly includes asymmetric terms in the Born–Oppenheimer diagonal correction. The HDO07 PES reproduces the observed rotation–vibration levels of HDO up to 25 000 cm^{-1} above the ground state with an rms error of 0.035 cm^{-1}. This number should be compared to equivalent rms errors of 0.45 cm^{-1} for the older, spectroscopically determined Partridge & Schwenke potential (Partridge & Schwenke 1997) and 1.9 cm^{-1} for the original *ab initio* CVRQD surface. Intensities were calculated using the recent *ab initio* CVR DMS (Lodi et al. 2008) which has been shown to give good results for both H_2O (Lodi et al. 2008; Lodi & Tennyson 2008; Lisak, Harvey & Hodges 2009) and HDO (Naumenko et al. 2008).

Nuclear motion calculations were performed with the DVR3D program suite (Tennyson et al. 2004) using Radau coordinates. Basis set parameters are those used by Yurchenko et al. (2008), where convergence tests were also performed.

HDO calculations are considerably more expensive than the corresponding one for H_2O for two reasons. First, the lowering of the symmetry leads directly to a doubling of the size of the various matrices that need to be diagonalized. Secondly, the increased mass of the D significantly increases the density of states so that any calculation covering a given energy range has to converge more states. Furthermore, each energy level in HDO is involved in twice as many transitions as each level in H_2O.

In this study, it was decided to retain all states up to 25 000 cm^{-1} above the vibrational ground state with rotational quantum number J up to 25 as these are important for lower temperature applications. For J between 26 and 50, states up to 17 600 cm^{-1} were retained. In practice, it is difficult to predict precisely how many states there will be up to a given energy, so these numbers are not precisely adhered to. Altogether we calculated 163 491 states by diagonalizing 101 separate Hamiltonian matrices, one for $J = 0$ and two for each J from 1 to 50. This gives a line list containing 697 454 528 transitions. These transitions should give a good representation of HDO spectra up to 3000 K.

As before, we separate the data into two files: an energy file containing the energies and associated quantum numbers, and a transitions file which contains pointers to the initial and final state in the energy plus the associated Einstein A coefficient, A_{if}. A sample of each of the energy file and the transition file is presented in Tables 1 and 2, respectively. For convenience of downloading, the transitions file is split into frequency regions. Table 3 gives these regions with the number of transitions in each region.

Table 1. Extract from the VTT levels file.

A	B	C	D	E	F	G	H	I	J	K
601	1	0	1	15.507 335	0	0	0	1	0	1
602	1	0	2	29.807 803	0	0	0	1	1	1
603	1	0	3	1419.053 467	0	1	0	1	0	1
604	1	0	4	1435.312 847	0	1	0	1	1	1
605	1	0	5	2738.945 608	1	0	0	1	0	1
606	1	0	6	2753.357 198	1	0	0	1	1	1
607	1	0	7	2797.612 146	0	2	0	1	0	1
608	1	0	8	2816.217 201	0	2	0	1	1	1
609	1	0	9	3722.889 801	0	0	1	1	0	1

A: row number in the file, B: J, C: symmetry, D: row number in the block, E: energy level in cm^{-1}, F, G, H: v_1, v_2, v_3. I, J, K: J, K_a, K_c.

Table 2. Extract from VTT transitions file.

A	B	C
101 055	105 028	1.12E-10
45 078	45 194	4.49E-08
48 581	52 548	3.39E-08
34 927	38 537	5.01E-08
77 863	67 370	2.97E-06
97 742	101 436	5.34E-07
44 578	45 171	1.43E-06
58 686	63 393	5.67E-07
63 224	55 979	7.61E-07
63 314	52 534	1.38E-07

A, B: row numbers in the levels file (upper and lower levels are not identified as the program tests for these). C: A_{if} (s^{-1}).

Table 3. Regions in cm^{-1} and numbers of transitions, N.

Region	N
000–250	25 194 444
250–500	24 751 485
500–750	24 159 509
750–1000	23 561 395
1000–1500	45 261 612
1500–2000	42 680 924
2000–2250	20 428 287
2250–2750	39 142 026
2750–3500	54 422 577
3500–4500	65 001 079
4500–5500	56 790 140
5500–7000	71 251 023
7000–9000	72 326 470
9000–14000	98 035 804
14000–20000	31 695 022
20000–26000	2 752 731
sum:	697 454 528

The quantity usually derived from observation is the line intensity, I, which has HITRAN units of cm molecule^{-1} (Rothman et al. 2009). I is temperature-dependent and is related to A_{if} by the expression

$$I = \frac{C(2J'+1)}{Q_{\rm vr}(T)\nu^2} \exp\left(\frac{-hcE''}{kT}\right)\left[1-\exp\left(\frac{-hc\nu}{kT}\right)\right] A_{if}, \quad (1)$$

where ν is the frequency in cm^{-1} and E'' is the energy of the lower rovibrational level in cm^{-1}. $Q_{\mathrm{vr}}(T)$ is the rovibrational partition function (see Hewitt et al. 2005), and is dimensionless. Boltzmann's constant, k, has units of JK^{-1} and the constant C has the value $(8\pi c)^{-1} = 1.3271 \times 10^{-12}\ \mathrm{s\,cm}^{-1}$.

It should be noted that the DVR3D programs use rigorous quantum numbers only, which for HDO are simply J, the total rotational angular momentum, and, p, the parity. Other conventional quantum numbers, such as vibrational labels (v_1, v_2, v_3) and asymmetric top rotational quantum numbers K_aK_c, are only approximate and have to be assigned by some other means.

Vibrational labels were assigned by calculating overlap integrals of the eigenfunctions with a set of model functions contracted as products of the one-dimensional solutions of the Schrodinger equation for HDO along the three vibrational coordinates (r_1, r_2 and θ). To assign the rotational quantum numbers, the wave functions of excited rovibrational states were compared with those of the ground vibrational state (000) and states (010) and (020), which were labelled by hand using program HAMFIT (see Petrakov & Scherbakov 2008) for J up to 15. The energy level file contains energies of 163 491 states, all of which have a complete set of rigorous quantum numbers. About 45 per cent of these levels also have unique, approximate quantum numbers; a further 45 per cent have non-unique approximate quantum numbers (e.g. the numbers are possibly repeated for another level); the final 10 per cent of the levels have no approximate assignment. The approximate quantum labels should be viewed with caution: only those associated with low-lying states can be regarded as secure.

3 RESULTS AND CONCLUSIONS

We present a number of synthetic spectra computed using the VTT line list to both confirm its accuracy and illustrate how the spectrum of HDO changes as a function of temperature. Starting first with room temperature, $T = 296$ K, spectra, we used the recently updated version of HITRAN (Rothman et al. 2009) as the source of reliable HDO data. These comparisons are all based on the assumption of pure HDO which means scaling spectra taken from HITRAN, which weights the transition intensities of HDO by 0.000 310 69 which corresponds to the terrestrial abundance of this isotopologue.

Fig. 1 gives an overview comparison of the VTT line list with HITRAN for infrared and visible wavelengths. As can be seen the agreement is generally very good and, unlike some other comparisons (Tennyson et al. 2009a; Yurchenko et al. 2009), it is also fairly complete. Fig. 2 gives a similar comparison for the far-infrared region where pure rotational transitions dominate the spectrum. As these figures are of too low resolution to illustrate accuracy, a sample higher resolution spectrum is given in Fig. 3.

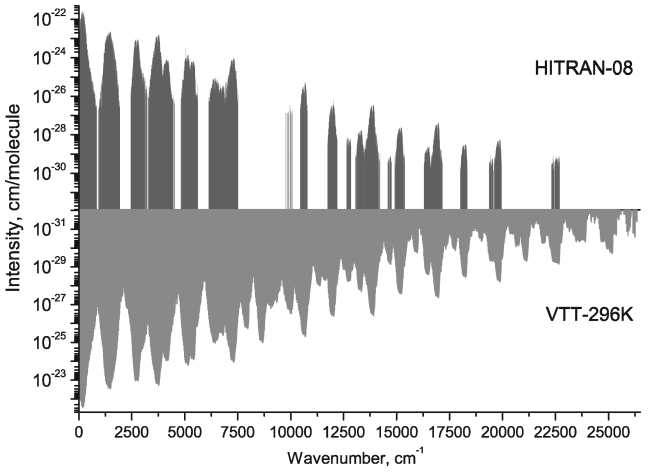

Figure 1. Overview comparison of HITRAN (Rothman et al. 2009) and VTT absorption spectra for pure HDO at 296 K.

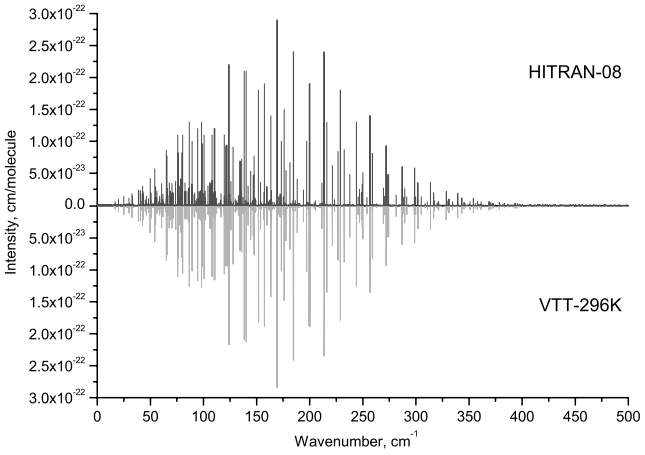

Figure 2. Comparison of HITRAN (Rothman et al. 2009) and VTT absorption spectra for pure HDO at 296 K in the far-infrared which is dominated by rotational transitions.

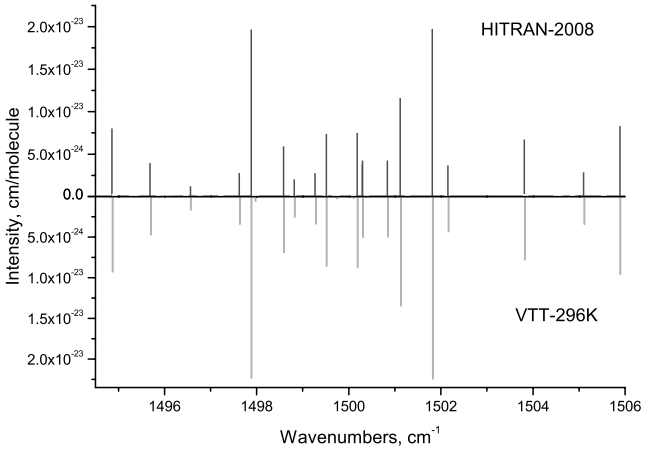

Figure 3. Detailed comparison of HITRAN (Rothman et al. 2009) and VTT absorption spectra for pure HDO at 296 K.

The main use of the VTT line list is for the synthesis and analysis of hot spectra. As mentioned above, there are very few laboratory measurements of hot HDO spectra. Fig. 4 compares the results from VTT with the 1773 K emission spectrum of Janca et al. (2003). It should be noted that Janca et al.'s spectrum does not give absolute intensities; it also gives fewer lines than we predict. The observation of fewer lines is partly a sensitivity issue but is also be due to the presence of both H_2O and D_2O in the experimental spectrum which leads to many HDO features being obscured or blended; furthermore, the high temperature means that many lines are significantly broadened. However, despite these issues, there is clearly very good agreement between our predictions and the observations.

Fig. 5 presents an overview of how the low-resolution absorption spectrum of HDO changes as a function of temperature. As can be seen, the number of HDO transitions increases rapidly with temperature to the extent that the spectrum takes on an almost blanket-like appearance at higher temperatures.

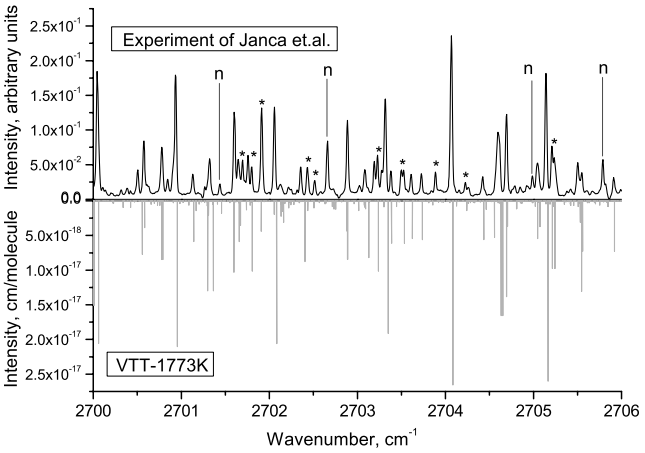

Figure 4. Detailed comparison of the observed HDO emission spectrum due to Janca et al. (2003) with a VTT emission spectrum calculated at 1773 K. Janca *et al.*'s measurements were performed in an H_2O/D_2O mixture and therefore contains lines due to both of these species. Experimental lines marked '*' belong to D_2O; those marked 'n' have not been assigned and may also not be due to HDO. The measured line intensities are in arbitrary units.

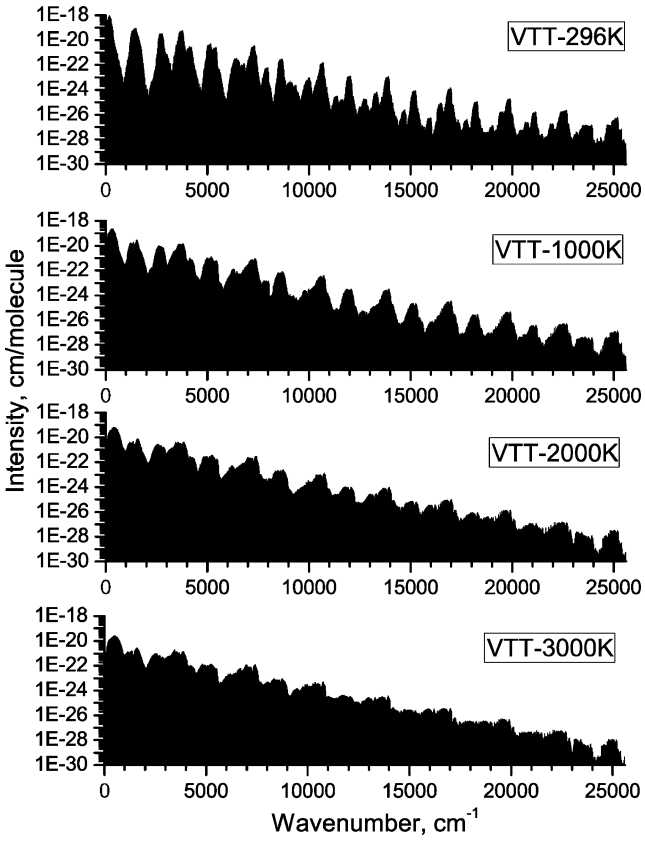

Figure 5. Absorption spectrum of HDO as a function of temperature using the VTT line list.

In summary, we present a newly computed line list for HDO which contains energy levels up to 25 000 cm^{-1} and rotational excitation up to $J = 50$. These yield nearly 700 million transitions. The line list and supporting files are made freely available in electronic form via ftp://cdsarc.u-strasbg.fr/cats/VI/127. The volume of data is such that the use of a workstation with at least 16 Gb RAM and running a 64-bit operating system is recommended; if this is an issue, please contact the lead authors. It is anticipated that this line list, which we call VTT, will become a valuable tool for astronomers, and others, interested in both the spectroscopy and modelling applications involving the deuterated water.

ACKNOWLEDGMENTS

This work was supported by the Royal Society via a Joint Project grant the EU under grant WWLC-008535. Calculations were performed at UCL; we thank UCL research computing and in particular Dr Jeremy Yates for assistance. We thank Olga Naumenko for comments on the manuscript. This work was performed as part of the Task Group of the IUPAC (Project No. 2004-035-1-100) on 'A data base of water transitions from experiment and theory'.

REFERENCES

Allard F., Hauschildt P. H., Miller S., Tennyson J., 1994, ApJ, 426, L39
Bailey J., 2009, Icarus, 201, 444
Banerjee D. P. K., Barber R. J., Ashok N. K., Tennyson J., 2005, ApJ, 672, L141
Barber R. J., Tennyson J., Harris G. J., Tolchenov R. N., 2006, MNRAS, 368, 1087
Barber R. J., Miller S., Dello Russo N., Mumma M. J., Tennyson J., Guio P., 2009, MNRAS, 398, 1593
Barletta P., Shirin S. V., Zobov N. F., Polyansky O. L., Tennyson J., Valeev E. F., Császár A. G., 2006, J. Chem. Phys., 125, 204307
Bejar V. J. S., Osorio M. R. Z., Rebolo R., 1999, ApJ, 521, 671
Bockelee-Morvan D. et al., 1998, Icarus, 133, 147
De Berg C., Bezard B., Owen T., Crisp D., Maillard J.-P., Lutz B. L., 1991, Sci, 251, 547
Dello Russo N., Bonev B. P., DiSanti M. A., Gibb E. L., Mumma M. J., Magee-Sauer K., Barber R. J., Tennyson J., 2005, ApJ, 621, 537
Fouchet T., Lellouch E., 2000, Icarus, 144, 114
Hewitt A. J., Doss N., Zobov N. F., Polyansky O. L., Tennyson J., 2005, MNRAS, 356, 1123
Janca A., Tereszchuk K., Bernath P. F., Zobov N. F., Shirin S. V., Polyansky O. L., Tennyson J., 2003, J. Mol. Spectrosc., 219, 132
Jorgensen U. G., Jensen P., Sorensen G. O., Aringer B., 2001, A&A, 372, 249
Joussaume S., Sadourny R., Jouzel J., 1984, Nat, 311, 24
Lisak D., Harvey D. K., Hodges J. T., 2009, Phys. Rev. A, 179, 052507
Lodi L., Tennyson J., 2008, J. Quant. Spectrosc. Radiat. Transf., 109, 1219
Lodi L. et al., 2008, J. Chem. Phys., 128, 044304
Montmessin F., Fouchet T., Forget F., 2005, J. Geophys. Res., 110, E03006
Naumenko O. V., Voronin B. A., Mazzotti F., Tennyson J., Campargue A., 2008, J. Mol. Spectrosc., 248, 122
Olofsson A. O. H. et al., 2007, A&A, 476, 791
Parekunnel T., Bernath P. F., Zobov N. F., Shirin S. V., Polyansky O. L., Tennyson J., 2001, J. Mol. Spectrosc., 101, 28
Partridge H., Schwenke D. W., 1997, J. Chem. Phys., 106, 4618
Pavlenko Y. V., Harris G. J., Tennyson J., Jones H. R. A., Brown J. M., Harrison J., Hill C., Yakovina L. A., 2008, MNRAS, 386, 1338
Petrakov A. V., Scherbakov A. P., 2008, Regularisation and Restriction of Decision Regions in the Vibration-Rotational Spectroscopy, Vol. 313. Tomsk Polytechnic University News, Tomsk (in Russian)
Polyansky O. L., Császár A. G., Shirin S. V., Zobov N. F., Barletta P., Tennyson J., Schwenke D. W., Knowles P. J., 2003, Sci, 299, 539
Rothman L. S. et al., 2009, J. Quant. Spectrosc. Radiative Transfer, 110, 533
Stark R. et al., 2004, ApJ, 608, 341
Tennyson J., Kostin M. A., Barletta P., Harris G. J., Polyansky O. L., Ramanlal J., Zobov N. F., 2004, Comput. Phys. Commun., 163, 85
Tennyson J., Harris G. J., Barber R. J., La Delfa S., Voronin B., Pavlenko Y. V., 2007, Molecular Phys., 105, 701

Tennyson J. et al., 2009a, J. Quant. Spectrosc. Radiat. Transf., 110, 533
Tennyson J. et al., 2009b, J. Quant. Spectrosc. Radiat. Transf., in press
Tinetti G. et al., 2007, Nat, 448, 169
Villanueva G. L., Mumma M. J., Bonev B. P., DiSanti M. A., Gibb E. L., Boehnhardt H., Lippi M., 2009, ApJ, 690, L5
Viti S., Tennyson J., Polyansky O. L., 1997, MNRAS, 287, 79
Viti S., Jones H. R. A., Richter M. J., Barber R. J., Tennyson J., Lacy J. H., 2008, MNRAS, 388, 1305
Voronin B. A. et al., 2007, J. Mol. Spectrosc., 244, 87
Yurchenko S. N., Voronin B. A., Tolchenov R. N., Doss N., Naumenko O. V., Thiel W., Tennyson J., 2008, J. Chem. Phys., 128, 044312
Yurchenko S. N., Barber R. J., Yachmenev A., Thiel W., Jensen P., Tennyson J., 2009, J. Phys. Chem. A, in press
Zobov N. F., Polyansky O. L., Le Sueur C. R., Tennyson J., 1996, Chem. Phys. Lett., 260, 381

This paper has been typeset from a TEX/LATEX file prepared by the author.