ExoMol molecular line lists: XI The spectrum of nitric acid

A.I. Pavlyuchko\textsuperscript{a,b}, S.N. Yurchenko\textsuperscript{a}, Jonathan Tennyson\textsuperscript{a}

\textsuperscript{a} Department of Physics and Astronomy, University College London, London, WC1E 6BT, UK; 
\textsuperscript{b} Moscow State University of Civil Engineering (MGSU), Russia, (pavlyuchko@rambler.ru)

ABSTRACT

Nitric acid is a possible biomarker in the atmospheres of exoplanets. An accurate line list of rotational and rotational-vibrational transitions is computed for nitric acid (HNO\textsubscript{3}). This line list covers wavelengths longer than 1.42 \(\mu\)m (0 – 7000 cm\(^{-1}\)) and temperatures up to 500 K. The line list is computed using a hybrid variational – perturbation theory and empirically tuned potential energy and dipole surfaces. It comprises almost 7 billion transitions involving rotations up to \(J = 100\). Comparisons with spectra from the HITRAN and PNNL databases demonstrate the accuracy of our calculations. Synthetic spectra of water – nitric acid mixtures suggest that nitric acid has features at 7.5 and 11.25 \(\mu\)m that are capable of providing a clear signature for HNO\textsubscript{3}; the feature at 11.25 \(\mu\)m is particularly promising. Partition functions plus full line lists of transitions are made available in an electronic form as supplementary data to the article and at www.exomol.com.

Key words: molecular data; opacity; astronomical data bases: miscellaneous; planets and satellites: atmospheres.

1 INTRODUCTION

The infrared spectrum of the nitric acid molecule, HNO\textsubscript{3}, is of astrophysical interest because of the growing interest in the study of atmospheres of extrasolar planets. In particular, this interest is particularly linked to that of the planets with earth-like atmospheres with a high content of nitrogen and oxygen. Nitric acid can be clearly observed in the earth’s atmosphere from space (Cooper et al. 2011) as it has a number of features which lie in water transparency windows. Its spectrum constitutes a possible biomarker as its existence is indicative of the presence of free oxygen and nitrogen, both of which lack strong spectral signatures at long wavelengths. It is also thought likely to pay an important role in nitrogen fixation on Mars and other earth-like planets (Summers & Khare 2007). It has also been suggested that \(\gamma\) -ray bursts could produce large quantities of HNO\textsubscript{3} in the atmospheres of earth-like planets (Thomas & Melott 2006). Nitric acid is a constituent of atmospheric ices on Earth and is thought likely to be present in the ice crust of Europa (Cooper et al. 2011). Its formation in interstellar ammonia ices has also been suggested (Zanchet et al. 2013), although nitric acid has yet to be observed in the interstellar medium.

Given the importance of HNO\textsubscript{3} in the earth’s atmosphere, its infrared spectrum has been well-studied in the laboratory. However, many of these spectra remain incompletely analysed with very few assignments to transitions at wavelengths shorter than 5 \(\mu\)m. This lack of assignment means that the spectra cannot be used for spectral simulations at temperatures other than the one of the original experiment. Spectral data on HNO\textsubscript{3} is only given in the HITRAN database (Rothman et al. 2013) for up to 1770 cm\(^{-1}\) (wavelengths longer than 5.6 \(\mu\)m). At shorter wavelength the Pacific Northwest National Laboratory (PNNL) database (Sharpe et al. 2004) provides infrared cross sections, but again these are only valid at the temperature for which they are recorded. Our results compare favourably with these sources, although this comparison shows both have their limitations (Pavlyuchko et al. 2015a).

The ExoMol project aims at generating comprehensive line observation and modelling atmospheres of exoplanets and other hot astronomical objects such as brown dwarfs and cool stars; its aims, scope and methodology have been summarised by Tennyson & Yurchenko (2012). The project has provided rotation-vibration line lists for a number of polyatomic molecules such as HCN (Barber et al. 2014), H\(_2\)S (Azzam et al. 2015), PH\(_3\) (Sousa-Silva et al. 2013), H\(_2\)CO (Al-Refaie et al. 2015) and CH\(_4\) (Yurchenko & Tennyson 2014; Yurchenko et al. 2014). None of these molecules contains more than two heavy atoms and the only pentatomic molecule considered, methane, has four hydrogens and high symmetry. It is clear that computing a comprehensive, temperature-dependent line list for HNO\textsubscript{3} represents a considerable computational challenge. To address this challenge we have developed a hybrid variational-perturbation theory procedure for computing spectra of such molecules (Pavlyuchko et al. 2015b) and...
have tested this for room-temperature nitric acid spectra (Pavlyuchko et al. 2015a). In this work we present a comprehensive line list for nitric acid which should be valid for temperatures up to 500 K. Given that nitric acid is only likely to exist in atmospheres which also contain water, we explicitly consider regions where HNO$_3$ spectra are likely to be observable in a humid atmosphere.

2 METHOD

Rotation-vibration line lists were generated using the program ANGMOL (Gribov & Pavlyuchko 1995, Pavlyuchko et al. 2015a). Although ANGMOL is designed to solve the nuclear motion problem for polyatomic molecules using a hybrid variational-perturbation theory method, it actually provides a complete environment for performing the line list calculations. ANGMOL automatically generates the inputs required to drive the appropriate ab initio electronic structure program, here the quantum chemistry package MOLPRO (Werner et al. 2012), to provide the necessary inputs for the nuclear motion calculations (potential energy, Hessian matrix and dipole moments). It also automatically adjusts both the potential energy surface (PES) and dipole moment function (DMF), which are represented as Taylor-expansions about equilibrium, to reproduce observed line positions and intensities using the method of regularisation (Tikhonov & Arsenin 1979, Gribov & Dementiev 1992). This method uses constraints provided by the initial ab initio calculations to allow many more parameters to be varied than there are experimental data. For full details of the fits and associated surfaces see Pavlyuchko et al. 2015a).

ANGMOL solves a Watson-like nuclear motion Hamiltonian expressed in internal curvilinear vibrational coordinates in three steps. First the rotation-less ($J = 0$) vibrational problem is solved in a basis of Morse oscillators for the stretches and harmonic oscillators for the bends by direct diagonalisation of a Hamiltonian matrix for low-lying vibrational states with contributions from higher states (basis functions) included using perturbation theory. In the second step, rotational problems for each vibrational state are solved using the eigenvectors from the vibrational problem and Wigner rotation matrices. An Eckart embedding is used to minimise Coriolis interactions which are again introduced using perturbation theory. The final step computes transition intensities; this step reduces the size of the calculation by predicting which transitions will be too weak to make a significant contribution and not calculating them. Transitions whose intensity is less than $10^{-12}$ km/molecule ($\approx 10^{-31}$ cm/molecule) were neglected. Integrals over the kinetic energy operator, PES and DMF are all simplified by the use of Taylor expansions for the operators. Here the PES and DMF were represented as fourth-order and second-order expansions, respectively. Further details of the calculation can be found in Pavlyuchko et al. 2015a).

Our aim was to compute a HNO$_3$ line list which is complete up to 7000 cm$^{-1}$ (longwards of 1.42 $\mu$m) for temperatures up to 500 K. For this we considered energy levels up to 9000 cm$^{-1}$ and rotational states with $J$ up to 100. $J = 100$ corresponds to a rotational excitation of about 2130 cm$^{-1}$.

The initial vibrational ($J = 0$) problem was solved using vibrational basis sets with polyad number 14. By this we mean that all combinations of functions were included when the sum of the orders of the polynomials was less than or equal to 14. The size of the basis required increases combinatorially with polyad number $N$; for HNO$_3$, which has 9 vibrational modes, the size of the basis is given by the binomial coefficient $\binom{N+9}{9}$ which equals 817 190 for $N = 14$ and 48 620 for $N = 9$. Matrices constructed with polyad 9 were explicitly diagonalised once the effects of higher states were included using perturbation theory, see Pavlyuchko et al. 2015a for further details. These calculations gave a total of 22 049 vibrational states below 9000 cm$^{-1}$.

Rotationally excited states were computed based on calculation which only considered up to polyad 7 but with the vibrational band origins fixed by the larger $J = 0$ calculation. This gave 9477 states lying below 7000 cm$^{-1}$ of which intensity considerations (see Pavlyuchko et al. 2015a) showed that only 1715 need to be considered explicitly. No transition whose intensity was less than $10^{-31}$ cm/molecule was considered.

Our final line list links 17 494 715 vibration-rotation energy levels with 6 722 136 109 transitions. Temperature-dependent partition functions for HNO$_3$ were calculated by explicitly summing all the calculated energy levels. Table 1 compares our results with those used by HITRAN (Fischer et al. 2003). The agreement is very good; our results are systematically slightly larger by less than 0.2% at low temperatures rising to 0.9% at 500 K. This increase is probably due to our better treatment of anharmonic effects, particularly in the large-amplitude, low-frequency OH torsional mode. A file containing the partition function 1 K steps for temperatures up to 500 K is given in supplementary material.

3 RESULTS

The line list contain almost 7 billion transitions. For compactness and ease of use, it is divided into separate energy level and transitions file. This is done using standard ExoMol format (Tennyson et al. 2013) which is based on a method originally developed for the BT2 line list (Barber et al. 2006). Extracts from

Figure 1. Comparison of our computed spectrum (Calc) with cross sections from the PNNL database (Sharpe et al. 2004) at a temperature of 298 K. Cross sections were generated from our line list using a Voigt profile with a Doppler and pressure broadening widths both set to 0.075 cm$^{-1}$.
Table 1. Partition function, $Q(T)$, HNO$_3$, as a function of temperature.

| $T$ (K) | This work | Fischer et al. (2003) |
|---------|-----------|-----------------------|
| 60      | 15632.60  | 15810                 |
| 110     | 37418.02  | 37374                 |
| 160     | 67172.12  | 67105                 |
| 210     | 107066.55 | 106880                |
| 260     | 161987.99 | 161650                |
| 310     | 239197.27 | 238250                |
| 360     | 348081.08 | 345830                |
| 410     | 500933.14 | 496570                |
| 460     | 713230.66 | 706730                |

Figure 2. Temperature-dependent absorption spectra of a nitric acid (smooth curve) and water vapour (spiky curve) mixture. Spectra are for 2% nitric acid at 300 K (upper) and 500 K (lower). The water spectra show a strong window around 4 µm.

Figure 3. Absorption spectrum of a nitric acid (regular set of lines) and water vapour (four strong lines) mixture in the 1330 – 1340 cm$^{-1}$ region. The spectrum is for 300 K with a concentration of 2% nitric acid.

Given that HNO$_3$ is being considered as possible biomarker and that any biomarker will probably have to be observed in a humid atmosphere, we consider a number of mixed water – nitric acid spectra. Figure 2 gives an overview of such spectra which have been constructed using water from HITRAN with 2% HNO$_3$ added for 300 K and 500 K. As is well-known, water absorptions dominate much of the infrared. However, HNO$_3$ features are clearly visible at about 7.5 µm and 11.2 µm. These are precisely where HNO$_3$ is clearly seen in our own atmosphere from space (Blecka & De Maziere 1996).

Figures 3 and 4 give detailed comparisons for the two regions in question. The spectrum in the 7.5 µm region shows a clear, regular spectral signature of HNO$_3$ but would require both a significant fraction of HNO$_3$ present and high resolution for a successful detection. When viewed in the Earth’s atmosphere this region also shows strong absorption lines due to CO$_2$, although there are not enough of these to mask the HNO$_3$. The 11.2 µm region is actually much more promising. The figure is drawn for only a trace concentration of HNO$_3$ (0.01% of water), much less than is present in the Earth’s atmosphere. Furthermore there is a distinct HNO$_3$ band centred about 11.25 µm and a feature 11.38 µm which should be visible (possibly blended together) at lower resolution. This would appear to be the most promising region for an HNO$_3$ detection. We note that there is one further HNO$_3$ band clearly visible in Fig. 2 at about 3 µm. This feature is a blend of the $2\nu_3$ overtone (band centre at 3404.4 cm$^{-1}$), and the $\nu_2 + \nu_4$ (2998.5 cm$^{-1}$) and $\nu_2 + \nu_3$ (3022.1 cm$^{-1}$) combination bands. This compound band sits in a window in the water spectrum but is not particularly prominent in the spectrum of the Earth’s atmosphere, presumably because it is actually significantly weaker than the features at 11.2 µm and 7.5 µm.

4 CONCLUSIONS

As part of the ExoMol project we have computed a comprehensive line list for the possible biomarker nitric acid applicable to temperatures up to 500 K. To do this we have had to develop a novel methodology capable of treat-
Table 2. Extract from the state file for HNO$_3$. Full tables are available from [http://cdsarc.u-strasbg.fr/cgi-bin/VizieR?-source=J/MNRAS/xxx/yy](http://cdsarc.u-strasbg.fr/cgi-bin/VizieR?-source=J/MNRAS/xxx/yy)

| n  | $\tilde{E}$ | g | J | $\Gamma$ | $v_1$ | $v_2$ | $v_3$ | $v_4$ | $v_5$ | $v_6$ | $v_7$ | $v_8$ | $v_9$ |
|----|---------|---|---|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1  | 0.000000 | 6 | 0 | A'     | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |
| 2  | 458.20000 | 6 | 0 | A''    | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 1   |
| 3  | 580.30000 | 6 | 0 | A'     | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 1   |
| 4  | 646.45000 | 6 | 0 | A'     | 0   | 0   | 0   | 0   | 0   | 0   | 1   | 0   | 0   |
| 5  | 763.10000 | 6 | 0 | A''    | 0   | 0   | 0   | 0   | 1   | 0   | 0   | 0   | 0   |
| 6  | 879.05000 | 6 | 0 | A'     | 0   | 0   | 0   | 1   | 0   | 0   | 0   | 0   | 0   |
| 7  | 896.30000 | 6 | 0 | A'     | 0   | 0   | 0   | 0   | 0   | 1   | 0   | 0   | 0   |
| 8  | 1038.00000| 6 | 0 | A''    | 0   | 0   | 0   | 0   | 0   | 0   | 1   | 1   | 0   |
| 9  | 1100.80000| 6 | 0 | A''    | 0   | 0   | 0   | 0   | 1   | 0   | 0   | 0   | 0   |
| 10 | 1148.97574| 6 | 0 | A'     | 0   | 0   | 0   | 0   | 0   | 1   | 0   | 0   | 2   |
| 11 | 1205.60000| 6 | 0 | A'     | 0   | 0   | 0   | 0   | 0   | 0   | 1   | 0   | 0   |
| 12 | 1213.85720| 6 | 0 | A'     | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 1   | 0   |
| 13 | 1275.72092| 6 | 0 | A'     | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 1   |
| 14 | 1289.00000| 6 | 0 | A'     | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 3   |
| 15 | 1303.10000| 6 | 0 | A'     | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |
| 16 | 1325.65000| 6 | 0 | A'     | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |
| 17 | 1340.60852| 6 | 0 | A''    | 0   | 0   | 1   | 0   | 0   | 0   | 0   | 0   | 0   |
| 18 | 1343.60000| 6 | 0 | A''    | 0   | 0   | 0   | 0   | 1   | 0   | 0   | 0   | 0   |
| 19 | 1403.87830| 6 | 0 | A''    | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 1   | 1   |
| 20 | 1450.28200| 6 | 0 | A'     | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 1   |

$n$: State counting number.  
$\tilde{E}$: State energy in cm$^{-1}$.  
g: State degeneracy.  
$J$: Rotational quantum number.  
$\Gamma$: Total symmetry.  
v$_1$, v$_2$, v$_3$, v$_4$, v$_5$, v$_6$, v$_7$, v$_8$, v$_9$: vibrational quantum numbers.

Figure 4. Absorption spectrum of a nitric acid (regular set of lines) and water vapour (isolated lines) mixture in the 875 – 900 cm$^{-1}$. The spectrum is for 300 K with a trace concentration of 0.01 % nitric acid.

Simulated spectra for a water-rich atmosphere suggest that there is real prospect of detecting trace quantities of nitric acid in the 11.25 $\mu$m region.

Table 3. Extracts from the transitions file for HNO$_3$. Full tables are available from [http://cdsarc.u-strasbg.fr/cgi-bin/VizieR?-source=J/MNRAS/xxx/yy](http://cdsarc.u-strasbg.fr/cgi-bin/VizieR?-source=J/MNRAS/xxx/yy)

| F  | I  | $A_{FI}$ |
|----|----|----------|
| 14516084 | 14516083 | 4.5130E-10 |
| 14516265 | 14516264 | 8.1767E-10 |
| 14515899 | 14515898 | 1.8398E-09 |
| 14516082 | 14516081 | 2.4872E-08 |
| 14516263 | 14516262 | 2.8596E-08 |
| 14515897 | 14515896 | 7.7843E-08 |
| 14516080 | 14516079 | 6.5506E-07 |
| 14516261 | 14516260 | 6.2021E-07 |
| 14515895 | 14515894 | 1.5810E-06 |
| 14516078 | 14516077 | 7.7309E-06 |
| 14516080 | 14516078 | 7.1042E-06 |
| 14515895 | 14515893 | 1.2759E-06 |
| 14516259 | 14516258 | 5.9759E-06 |
| 14515897 | 14515895 | 1.4427E-05 |
| 14515893 | 14515892 | 1.1427E-05 |
| 14516261 | 14516259 | 1.2759E-05 |

$F$: Upper state counting number;  
$I$: Lower state counting number;  
$A_{FI}$: Einstein-A coefficient in s$^{-1}$.

ACKNOWLEDGEMENTS

This work is supported by ERC Advanced Investigator Project 267219. The authors acknowledge the use of the UCL Legion High Performance Computing facility (Legion@UCL), and associated support services, in the completion of this work.

© 2012 RAS, MNRAS 000, 1–5
REFERENCES
Al-Refaie A. F., Yurchenko S. N., Yachmenev A., Tennyson J., 2015, MNRAS, 448, 1704
Azzam A. A. A., Yurchenko S. N., Tennyson J., 2015, MNRAS, (in preparation)
Barber R. J., Strange J. K., Hill C., Polyansky O. L., Mellau G. C., Yurchenko S. N., Tennyson J., 2014, MNRAS, 437, 1828
Barber R. J., Tennyson J., Harris G. J., Tolchenov R. N., 2006, MNRAS, 368, 1087
Blecka M. I., De Maziere M., 1996, Ann. Geophys., 14, 1103
Cooper M. et al., 2011, J. Geophys. Res., 116, D12306
Fischer J., Gamache R. R., Goldman A., Rothman L. S., Perrin A., 2003, J. Quant. Spectrosc. Radiat. Transf., 82, 401
Gribov L. A., Dementiev V. A., 1992, J. Appl. Spectr., 56, 709
Gribov L. A., Pavlyuchko A. I., 1998, Variational Methods for Solving Anharmonic Problems in the Theory of Vibrational Spectra of Molecules. Nauka, Moscow, (in Russian)
Hill C., Yurchenko S. N., Tennyson J., 2013, Icarus, 226, 1673
Pavlyuchko A. I., Yurchenko S. N., Tennyson J., 2015a, J. Chem. Phys., 142, 094309
Pavlyuchko A. I., Yurchenko S. N., Tennyson J., 2015b, Mol. Phys.
Rothman L. S. et al., 2013, J. Quant. Spectrosc. Radiat. Transf., 130, 4
Sharpe S. W., Johnson T. J., Sams R. L., Chu P. M., Rhoderick G. C., Johnson P. A., 2004, Appl. Spectrosc., 58, 1452
Sousa-Silva C., Al-Refaie A. F., Tennyson J., Yurchenko S. N., 2015, MNRAS, 446, 2337
Summers D. P., Khare B., 2007, Astrobiology, 7, 333
Tennyson J., Hill C., Yurchenko S. N., 2013, in AIP Conference Proceedings, Vol. 1545, 6th international conference on atomic and molecular data and their applications ICAMDATA-2012, AIP, New York, pp. 186–195
Tennyson J., Yurchenko S. N., 2012, MNRAS, 425, 21
Thomas B. C., Melott A. L., 2006, New J. Phys, 8, 120
Tikhonov A. N., Arsenin V. Y., 1979, Bull. Amer. Math. Soc. (N.S.), 1, 521
Werner H.-J., Knowles P. J., Knizia G., Manby F. R., Schütz M., 2012, WIREs Comput. Mol. Sci., 2, 242
Yurchenko S. N., Tennyson J., 2014, MNRAS, 440, 1649
Yurchenko S. N., Tennyson J., Bailey J., Hollis M. D. J., Tinetti G., 2014, Proc. Nat. Acad. Sci., 111, 9379
Zanchet A., Rodriguez-Lazcano Y., Galvez O., Herrero V. J., Escribano R., Mate B., 2013, ApJ, 777, 26