# Computational assignment of vibrational frequency bands facilitates the identification of interstellar peptides and spectroscopic parallaxes.

**Pardis Tabaee Damavandi, Richard W Pickersgill, Martin T Dove**

Queen Mary University of London, London, E1 4NS, UK

**Abstract** Spectroscopic parallax is the measure of the distance between two stars or celestial objects and relies on the stellar spectral type and luminosity class defined by the Morgan-Keenan classification system. UV, IR (Infrared), Raman or Optical spectrographic instruments are integrated in many telescopes and are used to obtain information on brightness, temperature (surface), density and velocities. Stars are classified based on their type and on their brightness, which allow us to obtain distances to them, however, with previous classification systems, the star’s size (dwarf, giant or supergiant) and composition (heavy metal versus carbon stars) were also used. The Morgan-Keenan classification offers information on the star colour (very blue, red) and the type, although the infrared wavelengths are approximately > 9000 Å, falling in the near-infrared range; spectra can be ulteriorly divided into continuous, band and linear. Band spectra are usually descriptive of molecular compounds and are the ones that we immersed in, by venturing an interpretation of the Raman-IR band spectra of neutral glycine (or NT glycine). Our method consisted in using vibrational dynamics (VD), the study of atomic oscillations within a molecule, after obtaining experimental vibrations for glycine through Raman or IR literature data. These techniques have been widely used in the past, along with X-ray or neutron scattering diffraction techniques, however, in recent years, researchers have used density functional theory, ab intio, or other computer simulation methods that facilitate band recognition. The goal of this work is to apply vibrational dynamics studies to the structure of NT glycine, and to then compare these values with its IR and Raman frequencies. By analyzing both simulation results and empirical data, we gain important information about the vibration modes of glycine. This study also shows that ‘invisible’ bands can be ‘detected’ with this technique. VD could therefore be used in the measurement of stellar abundances and to refine the quality of experimental Raman-IR data.

**Keywords** Vibrational Dynamics, Spectroscopy, Computational Astrobiology.

## 1. Introduction

Glycine is an essential amino acid that is the building block for more complex peptides (macromolecules) found in our organism, including haemoglobin, which plays a vital role as plasmatic binder, and glutathione (GSH), an excitatory neuromodulator involved in neurotransmission. Glycine is not only an indispensable component for our dietary intake, it is also employed pharmaceutically as an irrigator solution (1.5%) for transurethral resections of the prostate glands and blood tumours. The best method to distinguish glycine empirically is by IR absorption spectrophotometry as described by the specific monograph on the British Pharmacopoeia.

In light of this, we decided that this simple molecule is worth further scrutiny.

For years interstellar glycine (Combes 1996) has also been gaining major interest among astrophysicists craving to ‘single out’ extra-terrestrial forms of life. Kuan et al. (Kuan et al., 2003) conducted substantial spectral investigations consisting of ultraviolet photolysis and multisource observations in search of this amino acid on Orion KL and Sagittarius B2 (N-LMH). These studies led his group to detect 27 spectral lines for what they believed might have identified neutral (NT) Glycine. Although the work was later criticised (Snyder et al., 2005), in earlier years, the Murchison meteorite (Thaddeus, 2006; Shock et al., 1990; Martins et al., 2008) had revealed the presence of Glycine as its principal organic constituent. Later, in the same year as Kuan (2003), Bernstein et al. (Bernstein et al., 2003), carried out considerable analysis of the spectrum of amino- acetonitrile (Belloche et al., 2008), a parent molecule of glycine, and attempted the assignment of the vibrational frequencies on the

---

*Corresponding author.

E-mail address: p.tabaee@qmul.ac.uk (P. Tabaee Damavandi).

matrix isolated precursor compound. To achieve this, they compared density functional theory calculations with experimental Infrared (IR) spectra obtained under astrophysical conditions.

Similarly, we generated the vibrational frequencies for Glycine using the General Utility Lattice Program (GULP). This allows us to get the density of states for NT glycine, indicating its normal vibration modes per unit frequency, per unit volume. We then compared them with the Raman or IR experiments and simulations carried out by Bernstein and previous researchers (Ganesan et al., 2013; Krishnan et al., 2017; Rodriguez-Lazcano et al., 2012; Linder et al., 2008; Qian et al., 1994; Kumar et al., 2005).

## 2. Background

The classification of Stars based on their spectral type and on their luminosity class or composition warrants us an estimation of their distances. Vibrations can be used to analyse CNO abundances on Carbon-rich stars (Beers et al., 2007; Wahlin et al., 2006; Yamashita, 1966). Spectroscopic parallaxes (Russell et al., 1983), can then be calculated thanks to the Morgan-Keenan (MK) classification system (Keenan, 1985). UV, IR-Raman and optical spectrographic instruments integrated in telescopes enable us to gain details on brightness (Roman, 1952), surface, density and velocities. The MK classification offers information on the star colour and the type, however, the detected infrared wavelengths fall in the near-infrared (NIR) spectra range. Band spectra can be used to describe organic molecules, hereby, NT glycine. Despite Raman-IR spectroscopy data providing ‘empirical measures’ of atomic vibrations (Qian et al., 1994), computational chemistry can help (Reichenbächer et al. 2012). This review discusses the link between Raman-IR spectra and vibrational dynamics (VD) simulations performed on glycine. Our analysis of the phonon density of states of glycine and of its experimental data, convinced us that computational assignments (Peeters, 2004; Pendleton et al., 1994), and especially vibrational dynamics (Dove, 2011) simulations can be effective in Raman-IR spectra identification (Tabaee et al., 2016).

## 3. Methods

We initially built and optimised NT Glycine with CrystalMaker$^{TM}$ (version 9.2.1) and geometrically minimised the structure with the Northwest Computational Chemistry Package NWCHEM$^{TM}$ (version 6.1.1). ). We then used the wave functions for glycine to obtain the distributed multipole analysis (CamCASP$^{TM}$ version 5.8.7 with program GDMA2.2). From the multipoles we collected a best set of respective point charges, which can be achieved using the package MULFIT2.0$^{TM}$ (MULtipole-FITted charges).

The crystal structure of the amino acid (Fig. 1) was then taken from the CCDC (Cambridge Crystallographic Data Centre) database. Alternatively, the CDMS (Cologne database for Molecular Spectroscopy) can be used.

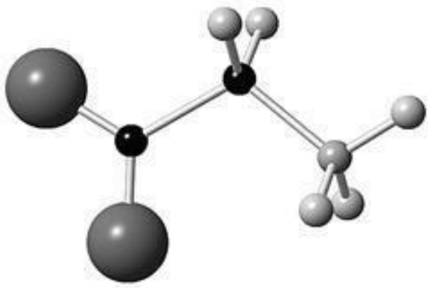

Fig. 1. Molecular structure of NT glycine. Spheres represent carbon (black), oxygen (dark gray), nitrogen (bluish gray) and hydrogen (light gray) atoms.

The conversion from the ‘crystal’ to the General Utility Lattice Program (GULP$^{TM}$) for the vibrational dynamics simulation, was reached with a Convertor (Tabaee et al., 2016). All the simulations were run at constant pressure and NT Glycine was particularly optimised at constant pressure, and its vibrational frequencies (cm$^{-1}$) were calculated for the final geometry with GULP$^{TM}$ (Gale et al., 2017). An Ewald Summation method was chosen for the calculation. The vibrational modes were finally compared with experimental data from the literature.

## 4. Vibrational Dynamics of Glycine

As mentioned above, after performing a VD analysis on NT Glycine (Fig. 2) we compared its vibrational frequencies with its Raman-IR spectra (Table 1).

---

*Corresponding author.

E-mail address: p.tabaee@qmul.ac.uk (P. Tabaee Damavandi).

| Frequencies (cm$^{-1}$) | | | |
|---|---|---|---|
| GULP calculations | Experimental IR /Raman spectra | Standard deviation | Assignment |
| 106 | | | C-N-C deformation |
| 265 | 303 | 0.707 | C-N-C deformation |
| 530 | 522 | 5.66 | C-O-O rock |
| 689 | 682 | 4.95 | C-N torsion |
| 848 | 828 | | C-N-C stretch |
| 954 | 953 | 0.707 | CH-NH wag |
| 1007 | 1013 | 4.24 | CO tors. (carboxyl) |
| 1378 | 1373 | 3.54 | HCH, CN, CO, CC str. |
| 1537 | 1537 | 0 | $NH_2$ scissors, CN |
| 1696 | | | CH, NH stretches |
| 1802 | | | CO str., OH bend |
| 2597 | | | C-H stretch |
| 2915 | 2907 | 5.66 | C-H stretch |
| 2968 | 2969 | 0.707 | C-H asym., stretch |
| 3233 | | | NH stretch |
| 3339 | 3348 | 6.36 | OH, NH stretches |

Table 1. The table illustrates key modes matching the experimental Raman-IR spectra (Linder et al, 2008; Qian et al., 1994) with the VD calculations (GULPTM).

Basic analogies between the experimental data and the VD (Table 1) are spotted. Firstly, the main C-H stretch peak is found at a frequency of 2968 cm$^{-1}$. Further C-H stretch modes can be viewed between 2014-2968 cm$^{-1}$, analogously to what reported by Linder et al. (Linder et al., 2008) and various researchers (Qian et al., 1994). C-N stretches and C-O torsions can be grasped at around 1007-1378 cm$^{-1}$. We also identified the glycine C-O stretches at 1802 and 3339 cm$^{-1}$, the carboxylic group region at 530 cm$^{-1}$ and the NH-CH wag at 954 cm$^{-1}$; these values can be likened to previous findings. Accordingly, the $NH_2$ scissors and C-N stretches correspond to the same frequency at 1537 cm$^{-1}$. All these observations indicate that vibrational frequencies can be compared to IR/Raman experimental methods and can be used to facilitate IR/Raman assignments.

Although we don't provide spectroscopic parallax calculations, we hereafter encourage the prospective use of computational software, particularly of vibrational dynamics in support of astronomical empirical research.

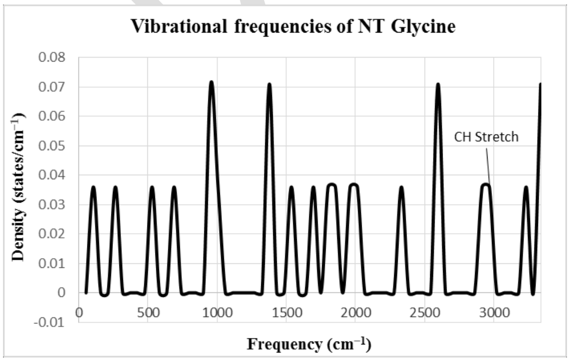

Fig. 2. Vibrational frequencies of NT Glycine generated with the General utility lattice program. Several modes are depicted indicating the disorder and therefore flexibility of glycine. The C-H stretch peak (2968 cm$^{-1}$) is clearly visible. It can be noted that the peaks are very neat and not 'noisy'.

## Acknowledgments

We would like to thank the following researchers for their contributions, Dr Andrei Sapelkin (Queen Mary University of London), Dr Alston J Misquitta (MULFIT), Prof Asa H Barber (London South Bank University), Prof Philip J Camp (University of Edinburgh), Massy Habibpour and D. Nummey

*Corresponding author.

E-mail address: p.tabaee@qmul.ac.uk (P. Tabaee Damavandi).

# REFERENCES

Beers T. C., Near-Infrared Spectroscopy of Carbon-Enhanced Metal-Poor Stars. I. A SOAR/OSIRIS Pilot Study, The Astronomical Journal, 133, 1193-1203, 2007.

Belloche A., Menten K. M., Comito C., Müller H. S. P. et al., Detection of amino acetonitrile in Sgr B2(N), Astronomy & Astrophysics, 482, 179-196, 2008.

Bernstein M. P., The infrared spectrum of matrix isolated amino acetonitrile, a precursor to the amino acid glycine, Advances in Space Research, 33, 40–43, 2004.

Combes F., Search for interstellar glycine, Astron. Astrophys., 308, 618-622, 1996.

Dove M. T. Introduction to the theory of lattice dynamics, EDP Sciences, 12, 123-159, 2011.

Gale J. D. General Utility Lattice Program version-3.4 (Manual), 50-51, (Last updated-2017).

Ganesan, A., Brunger M. J. & Wang F., A study of aliphatic amino acids using simulated vibrational circular dichroism and Raman optical activity spectra, Eur. Phys. J. D, 67, 229, 2013.

Keenan P.C., The MK Classification and its Calibration, Calibration of Fundamental Stellar Quantities, 111, 121-136, 1985.

Krishnan Y., Vincent A. & Paranjothy M., Classical dynamics simulations of interstellar glycine formation via CH2=NH+CO+H2OCH2=NH+CO+H2O reaction, Journal of Chemical Sciences, 129(10), 1571–1577, 2017.

Kuan Y-J., Charnley S. B., Huang H-C. et al., Interstellar Glycine, The Astrophysical Journal, 593, 848-867, 2003.

Kumar S., Rai A. K., Singh V.B. et al., Vibrational spectrum of glycine molecule, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 61(11–12), 2741-2746, 2005.

Linder R. et al., Gas phase infrared spectra of nonaromatic amino acids, Chemical Physics Letters 453, 1–6, 2008.

Martins Z., Botta O., Fogel M. L., Extraterrestrial nucleobases in the Murchison meteorite, Earth and Planetary Science Letters, 270, 130-136, 2008.

Peeters E., The Unidentified InfraRed Features after ISO, Astro- physics of Dust, ASP Conference Series, 309, 141-158, 2004.

Pendleton Y. J. Sandford, S. A., Allamandola, L. J. et al., Near-infrared absorption spectroscopy of interstellar hydro- carbon grains, Astrophysical Journal, Part 1, 437(2), 683-696, 1994.

Qian W., Krimm S. Vibrational analysis of glutathione, Biopolymers, 34(10), 1377-1394, 1994.

Reichenbächer M., Popp J. Challenges in Molecular Structure Determination, Springer, XX(482), 64-143, 2012.

Rodriguez-Lazcano Y., Maté B., Gálvezet Ó. et al., IR spectroscopic signatures of solid glycine and alanine in astrophysical ices, European Planetary Science Congress, 7, 127, 2012.

Roman N. G., The spectra of the Bright Stars of types F5-K5, Astrophysical Journal, 116, 122, 1952.

Russell H. N. & Moore C. E., A Comparison of Spectroscopic and Trigonometric Parallaxes, Astrophysical Journal, 87, 389, 1983.

Shock E. L., Schulte M. D., Summary and implications of reported amino acid concentrations in the Murchison meteorite, Geochim Cosmochim Acta., 54(11), 3159-7, 1990.

Snyder L. E., Lovas F. J., Hollis J. M. et al., A RIGOROUS AT- TEMPT TO VERIFY INTERSTELLAR GLYCINE, The Astrophysical Journal, 619, 914–930, 2005.

Tabaee Damavandi P. et al. (2016), Doctoral Thesis. Novel applications of vibrational dynamics in the study of protein misfolding and neurodegenerative disorders [27 September 2016].

Thaddeus P., The prebiotic molecules observed in the interstellar gas. Philos Trans R Soc Lond B Biol Sci., 361(1474): 1681–1687, 2006.

Wahlin R., Eriksson K., Gustafsson B., Hinkle K. H. et al., Phoenix Spectra of Carbon Stars in the LMC, High Resolution Infrared Spectroscopy in Astronomy, ESO Astrophysics Symposia. Springer, Berlin, Heidelberg, 439-442, 2006.

Yamashita Y., A STUDY OF CARBON-STAR SPECTRA BASED ON THE C-CLASSIFICATION, Publ. of the Dominion Astrophysical Observatory, XIII(5), 67-98, 1966.

---

*Corresponding author.

E-mail address: p.tabaee@qmul.ac.uk (P. Tabaee Damavandi).

---

*Corresponding author.

E-mail address: p.tabaee@qmul.ac.uk (P. Tabaee Damavandi).