Interstellar tryptophan revisited

Reggie L. Hudson⋆

Astrochemistry Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD, 20771, USA

ABSTRACT

A recent assignment of the amino acid tryptophan to infrared emission lines in the gas of the IC 348 star cluster is re-examined. A comparison of spectra from the *Spitzer* Telescope to laboratory data shows that there is no firm support for the tryptophan assignment. Suggestions are made for future observational searches for tryptophan and for supporting laboratory work.

Key words: astrochemistry – methods: laboratory: molecular – methods: laboratory: solid state – ISM: molecules – infrared: ISM.

1 INTRODUCTION

The detection and identification of biologically relevant molecules in the interstellar medium continues to be of high interest. This is readily seen through two recent papers related to interstellar amino acids, both in this journal, one paper on glycine (Carl et al. 2023) and the other on tryptophan (Iglesias-Groth 2023). Structures for the two molecules are shown in Fig. 1. The paper of Carl et al. (2023) was a continuation of glycine work from 20 yr ago by some of the authors (Kuan et al. 2003), the recent study being a search for the glycine molecule at 70–78 GHz in a dark interstellar cloud. Only an upper limit on glycine abundance was found (i.e. no identification). In contrast, the paper by Iglesias-Groth (2023) reported a detection of tryptophan at infrared (IR) wavelengths ($\lambda \approx 10$–33 μm, $\tilde{v} \approx 1000 - 303$ cm^{-1}) using archived spectra from the *Spitzer* Space Telescope, the *Spitzer* data being compared to the author's laboratory spectra of tryptophan. The IR source for the *Spitzer* spectra was the gas of the star cluster IC 348.

Since the smaller glycine molecule of Fig. 1 has yet to be found in the interstellar medium, any claim of an interstellar presence for the larger tryptophan molecule immediately raises questions. Moreover, none of the three molecules of Fig. 2, which can be considered components of tryptophan, have been identified in the interstellar medium. Tryptophan also has not been identified in meteoritic samples (e.g. Glavin et al. 2020). With these points in mind, and in light of our interest in amino-acid chemistry and spectroscopy (e.g. Hudson et al. 2009; Gerakines et al. 2012), we have re-examined the recent work on interstellar tryptophan published here. Our conclusion is that no identification of tryptophan is possible from the results reported.

2 SPECTRA

As in the study of Iglesias-Groth (2023), hereafter denoted IG23, only spectra and results already in print or otherwise publicly available were used in this work. An IR spectrum of tryptophan dispersed in

KBr was taken from the National Institute of Standards and Technology Chemistry WebBook (https://webbook.nist.gov/chemistry/). We also used several of the spectra in the paper of IG23, including some *Spitzer* data, and a few spectra from the literature (Cao & Fischer 1999; Matei et al. 2005), mainly for comparisons of results from different sources. No significant differences were found among the IR spectra of tryptophan dispersed in solids and recorded at room temperature.

3 RESULTS

The tryptophan assignment of IG23 was based on a comparison of *Spitzer* spectroscopic data with IR positions of tryptophan in solid-phase spectra. The two types of spectra were not presented together in a single figure, so in our Fig. 3 we show them adjacent to one another. It is immediately obvious that the *Spitzer* spectra, the upper trace in each panel, are highly pixelated, with features closer than about 0.01 μm being almost impossible to resolve and with almost no information available about the shapes and widths for most of the lines observed, the exception being a large polycyclic aromatic hydrocarbon (PAH) emission feature at 11 .2 μm (Allamandola et al. 1985). The *Spitzer* traces also show an IR "peak" of some type at almost every wavelength in the two spectra. It is difficult to know if any such feature is due to one particular molecule or ion or to overlapping bands from more than one chemical species.

Another observation that quickly can be made with Fig. 3 is that in neither panel is there convincing agreement between the laboratory spectrum and that from *Spitzer*. The peak positions of tryptophan in the two reference spectra are hardly suggestive, if at all, of any distinctive features of the molecule in the two *Spitzer* traces. Note that the wavelength regions of Fig. 3 were selected because they were the two reported by IG23 as containing the tryptophan emissions with the *highest* fluxes, at 11.57 and 13.44 μm (i.e. the regions reported as showing the *tallest* alleged tryptophan peaks).

4 DISCUSSION

A major difficulty in the recent assignment of IR features in the *Spitzer* spectra of Fig. 3 to tryptophan is the lack of a suitable
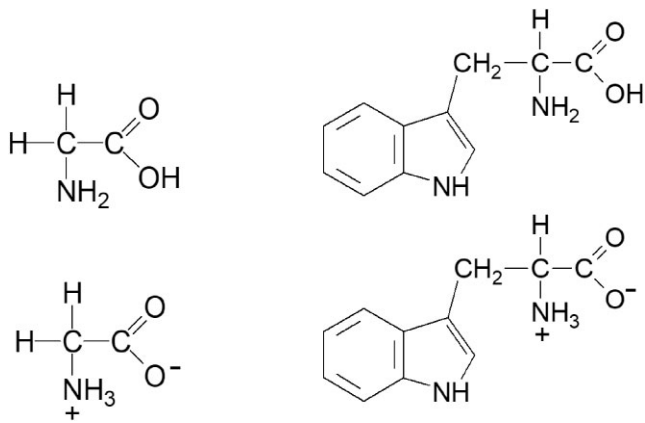
⋆ E-mail: reggie.hudson@nasa.gov

Figure 1. Structures of glycine (left) and tryptophan (right). The top row has the non-zwitterionic forms, the bottom row has the zwitterionic forms.
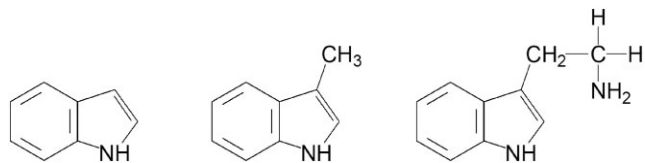

Figure 2. From left to right, structures of indole, 3-methylindole, and tryptamine.
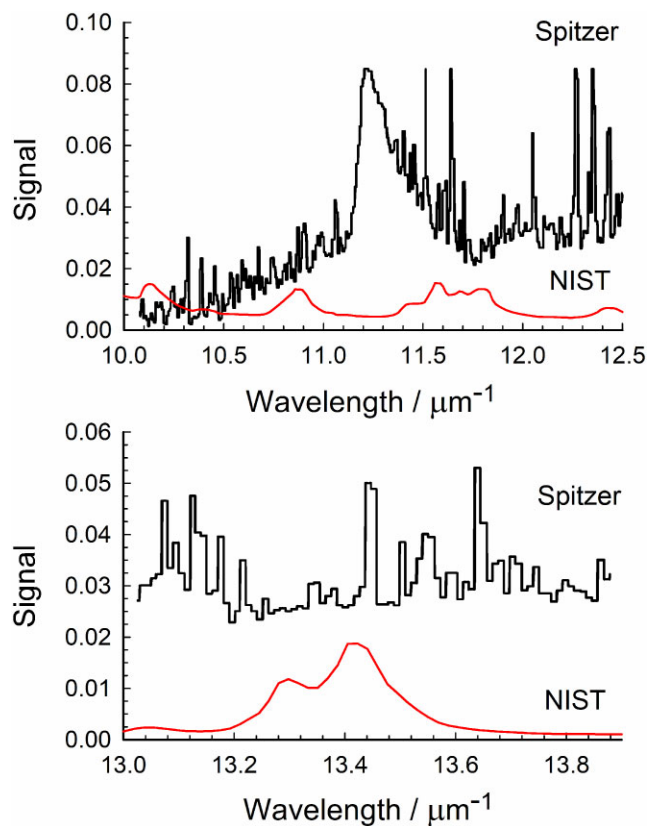

Figure 3. Two regions of the IR spectrum of IC 348 from the *Spitzer* Space Telescope (upper trace in each panel) compared to room-temperature reference spectra of crystalline tryptophan (lower trace in each panel) from the NIST Chemistry WebBook. The signal (flux) for the *Spitzer* data is in janskys. The signal (absorbance) of the NIST spectrum has been divided by 10 in the upper panel and by 50 in the lower panel.

reference spectrum. There is no reason to believe that gas-phase emission wavelengths of tryptophan will be matched by solid-phase absorption wavelengths. Appropriate IR reference spectra provide critical constraints on any spectral assignment, such as peak positions, band shapes, line widths, IR intensities, and variations in these with temperature. Without these constraints, robust IR assignments are extremely difficult. Going further, IR identifications in extraterrestrial ices of molecules with more than about eight atoms are challenging, but firm identifications of gas-phase molecules using only solid-phase reference spectra would seem nearly impossible.

A separate issue concerns differences in molecular structure. Gas-phase tryptophan has been studied and its molecular structure found to be that shown in the first row of Fig. 1 (e.g. Snoek et al. 2001), aside from conformational variations. However, tryptophan in a solid form at room temperature adopts the zwitterionic structure in the bottom row of Fig. 1. This means that gas-phase interstellar tryptophan molecules, if they exist, will not have the same structure as the molecules used to prepare the laboratory samples for the reference spectra in Fig. 3 and for the comparisons to *Spitzer* spectra in IG23. The differences in structure mean that the vibrational modes of the two forms of tryptophan in Fig. 1 will not necessarily be the same (See Maté et al. 2011 and Gerakines et al. 2012 for examples). Therefore, a safer tryptophan comparison for *Spitzer* data is to gas-phase IR spectra such as those of Bakker et al. (2003). Those authors report that the strongest tryptophan line between about 20 and 29 μm (500 and 350 cm^{-1}) is near 25 μm (400 cm^{-1}) in three different conformational isomers, including the most stable. However, no strong feature is seen there in the *Spitzer* spectra of Iglesias-Groth & Marin-Dobricic (2023).

Another complication concerns the calculation of molecular abundance. The column densities derived in IG23 for gas-phase, non-zwitterionic tryptophan were based on integrated IR band strengths of zwitterionic tryptophan dispersed in a solid matrix (Iglesias-Groth & Cataldo 2021). Aside from the questionable validity of using solid-phase IR intensities to calculate gas-phase abundances, there is a question of how those same solid-phase intensities were determined. The usual practice for measuring an IR band strength in a solid requires samples of different thickness or concentration to be prepared, absorbances of each to be measured, and a graph of absorbance as a function of thickness or concentration to be constructed. The slope of such a Beer's Law calibration curve is then used to calculate a band strength (e.g. Hollenberg & Dows, 1962; Bouilloud et al. 2015; Yarnall et al. 2020).

Unfortunately, the abundance calculations of IG23 appear to be based on a single tryptophan sample. With only one data point it is, of course, impossible to draw a calibration curve, examine its linearity, check for a zero intercept, extract a slope, and estimate the resulting band strength's uncertainty from that slope. No integration ranges were reported for those same earlier tryptophan band strength results and no details were provided as to how overlapping IR features were separated, if they were (Iglesias-Groth & Cataldo 2021). Finally, it cannot be determined if spectral bands are saturated if only one sample is examined, which greatly reduces the confidence in any accompanying IR intensity results.

5 CONCLUSIONS AND FUTURE WORK

The IR evidence presented to date for interstellar tryptophan is not convincing. The IR spectral assignment is severely hindered by the lack of a published comparison of the *Spitzer* data to a gas-phase tryptophan spectrum with accurate gas-phase peak positions and intensities, which are fundamental to any IR identification. Future

studies should make such a comparison and also recognize that tryptophan can exist in several conformations in both the solid and gas phases (Cao & Fischer 1999; Bakker et al. 2003). We note that a rotational spectrum of tryptophan has been published (Sanz et al. 2014), which could aid in the search for this interesting molecule. Rotational spectra of the smaller components of tryptophan shown in Fig. 2 also have been reported, indole (Vávra et al. 2019), 3-methylindole (Remmers et al. 1997), and tryptamine (Caminati 2004). It also would be useful for the photolytic and radiolytic stability of tryptophan to be measured, as it has been for several other amino acids (e.g. Gerakines et al. 2012; Johnson et al. 2012; Portugal et al. 2014). Finally, it would be interesting to determine if tryptamine (Fig. 2) undergoes radiolytic carboxylation at cryogenic temperatures to make tryptophan.

The lure and importance of extraterrestrial amino acids is great, but tryptophan has not yet been identified. Future investigations are encouraged.

AUTHOR DISCLOSURE STATEMENT

Author declares that there is no conflict of interest.

ACKNOWLEDGEMENTS

DATA AVAILABILITY

The data underlying this article will be shared on reasonable request to the author.

REFERENCES

Allamandola L., Tielens A., Barker J., 1985, ApJ, 290, L25

Bakker J. M., Aleese L., Meijer G., von Helden G., 2003, Phys. Rev., 91, 203003

Bouilloud M., Fray N., Bénilan Y., Cottin H., Gazeau M.-C., Jolly A., 2015, MNRAS, 451, 2145

Caminati W., 2004, Phys. Chem. Chem. Phys., 6, 2809

Cao X., Fischer G., 1999, J. Phys. Chem. A, 103, 9995

Carl T., Wirström E., Bergman P., Charnley S. B., Kuan Y.-J., 2023, MNRAS, 524, 5993

Gerakines P. A., Hudson R. L., Moore M. H., Bell J.-L., 2012, Icarus, 220, 647

Glavin D. P., Burton A. S., Elsila J. E., Aponte J. C., Dworkin J. P., 2020, Chem. Rev., 130, 4660

Hollenberg J. L., Dows D. A., 1962, J. Chem. Phys., 37, 1300

Hudson R. L., Lewis A. S., Moore M. H., Dworkin J. P., Martin M. P., 2009, Enigmatic Isovaline: Investigating the Stability, Racemization, and Formation of a Non-Biological Meteoritic Amino Acid. Astron. Soc. Pac., San Francisco, California, USA

Iglesias-Groth S., 2023, MNRAS, 523, 2876

Iglesias-Groth S., Cataldo F., 2021, Astrobiology, 21, 526

Iglesias-Groth S., Marin-Dobricic M., 2023, MNRAS, 521, 2248

Johnson P. V., Hodyss R., Chernow V. F., Lipscomb D. M., Goguen J. D., 2012, Icarus, 221, 800

Kuan Y.-J., Charnley S. B., Huang H.-C., Tseng W.-L., Kisiel Z., ApJ, 2003, 593, 848

Maté B., Rodriguez-Lazcano Y., Gálvez Ó., Tanarro I., Escribano R., 2011, Phys. Chem. Chem. Phys., 13, 12268

Matei A. D., Drichko N., Gompf B., Dressel M., 2005, Chem. Phys., 316, 61

Portugal W., Pilling S., Boduch P., Rothard H., Andrade D. P. P., 2014, MNRAS, 441, 3209

Remmers K., Jalviste E., Mistrı´k I., Berden G., Meerts W. L., 1997, J. Chem. Phys., 108, 8436

Sanz M. E., Cabezas C., Mata S., Alonso J. L., 2014, J. Chem. Phys., 140, 204308

Snoek L. C., Kroemer R. T., Hockridge M. R., Simons J. P., 2001, Phys. Chem. Chem. Phys., 3, 1819

Vávra K., Luková K., Kania P., Koucký J., Urban Š., 2019, J. Mol. Spec., 363, 111175

Yarnall Y. Y., Gerakines P. A., Hudson R. L., 2020, MNRAS, 494, 4606

This paper has been typeset from a Microsoft Word file prepared by the author.