#### Journal of Molecular Spectroscopy 377 (2021) 111422

Contents lists available at ScienceDirect

# Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

# Theoretical rovibrational characterization of HAINP: Weak bonding but strong intensities

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#### ARTICLE INFO

Article history: Received 2 November 2020 In revised form 10 January 2021 Accepted 12 January 2021 Available online 6 February 2021

Keywords: Astrochemistry Infrared spectroscopy Rotational constants Coupled cluster theory Vibrational perturbation theory

#### ABSTRACT

In the search for interstellar molecules containing at least one Al—H bond, HAlNP may be a viable candidate for potential observation. The present high-level quantum chemical analysis shows that the 1 <sup>1</sup>A' and 1 <sup>3</sup>A" states of HAINP are nearly degenerate (differ by ~ 20 cm<sup>-1</sup>). Additionally, this molecular connectivity is preferred over the resulting van der Waals AlH…PN isomer by 17.31 kcal/mol and has exceptionally bright itensities for fundamental infrared frequencies at 1763.2 cm<sup>-1</sup> and 1261.6 cm<sup>-1</sup> for the singlet as well as 1813.1 cm<sup>-1</sup> and 1296.2 cm<sup>-1</sup> in the triplet. These sets both fall in regions perceived to be dominated by hydrocarbon emissions, but the notable strengths of these infrared signals imply that this molecule or other third-row atom containing species cannot be fully neglected for inclusion as potential, astronomical, spectral carriers. 1 <sup>1</sup>A' HAINP also possesses a 0.95 D dipole moment and near-prolate behavior with a trusted CCCR  $B_{eff}$  of 3056.8 MHz. Finally, the 1 <sup>3</sup>A' state vibrational frequencies computed via two different coupled cluster approaches (CCSD(T)-F12/cc-pVTZ-F12 and CcCR) agree to, typically, within 2.5 cm<sup>-1</sup> of one another giving future promise for the former's use in larger molecules where CcCR is intractable.

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### 1. Introduction

Of the few aluminum-bearing molecules observed in various astrophysical regions, none, surprisingly, contain an Al—H bond, as of yet [1]. The closest are the AlF and AlCl aluminum halides [2,3], along with AlOH [4] with the oxygen separating the aluminum and hydrogen. Speculation has arisen that the hydrogen preferentially binds to the oxygen when reacting with the astrophysically-known AlO diatomic [5], or AlO nearly exclusively dissociates as aluminum atoms and hydroxyl radicals upon collision with a hydrogen atom [6] and likely goes on to form aluminum oxide dust and nanocrystals [7]. While recent work has shown that Al forms strong bonds with oxygen [8], aluminum also forms only slightly weaker bonds with nitrogen [9,10]. Consequently, other molecules containing Al—H bonds may be present in various astrophysical regions, but they may likely require an absence of oxygen in their composition.

One molecule that fits this description is HAINP. An Al—H bond is present as is an Al—N bond. Additionally, PN has been observed in various astronomical sources for more than 30 years [11,12].

\* Corresponding author. E-mail address: r410@olemiss.edu (R.C. Fortenberry). While analogous to the difficult-to-observe  $N_2$  molecule, the heteronuclear construction of PN and the "reluctance to hybridize" in phosphorus [13] unbalances the electron cloud likely allowing for stronger bonding than is present in molecular structures with  $N_2$  ligands [14]. While both Al and P are underabundant compared to Si and S [15], they are still atoms present in known molecules observed in various astrophysical media. Furthermore, the interstellar roster of phosphorus-bearing molecules is nearly empty for tetraatomic species and larger (save for PH<sub>3</sub> [16,17]). Hence, additional, promising candidates containing this atom necessary for both life and geology, as we know each, would help to elucidate larger chemical pathways of the interstellar medium (ISM), protoplanetary disks, or other regions where they may be found. Experimental isolation of many molecules is rather challenging

Experimental isolation of many molecules is rather challenging for generating data useful for comparison to radioastronomical or infrared astrophysical observations. However, the barrier to this is greatly lowered when high-level quantum chemical data are on hand to provide excellent predictions as to the needed physical quantities. One of the best methods for producing such data over the past decade has been quartic force fields (QFF) conjoined to highly-accurate coupled cluster electronic structure theory computations [18–22]. The former are fourth-order Taylor series expansions of the potential within the Watson Hamiltonian [23].







The latter most often use the singles, doubles, and perturbative triples level [CCSD(T)] [24–26] and make considerations for complete basis set (CBS) extrapolations, core electron correlation, and scalar relativity [27] in the CcCR composite QFF [28]. Additionally, much less costly QFFs involving the more recently developed explicitly correlated theories in CCSD(T)-F12 [29,30] have been shown to produce vibrational frequencies nearly as accurate as their CcCR counterparts [31–33] even if the rotational constants suffer somewhat. In either case, vibrational frequencies are typically accurate to within 5 cm<sup>-1</sup> or better of experiment, while the CcCR rotational constants for tetraatomics and larger are in error by less than 20 MHz (or 0.12%) [28].

Consequently, the present work will utilize both the CcCR and CCSD(T)-F12-based QFFs to produce fundamental vibrational frequencies and spectroscopic constants for the HAINP molecule. These should then aid in any laboratory characterization of this molecule. The available experimental data for AlOH are in excellent agreement with the recently-reported CcCR rotational constants [8,34]. As a result, the data provided herein should be similarly accurate and may help to add to the list of possible interstellar aluminum-bearing (and phosophorus-bearing) molecules as has been done recently in our groups for [Al, N, C, O] isomers [10] and OAlOH [8]. The growth of ground-based radio observatories such as the Atacama Large Millimeter Array (ALMA) and space-based infrared observatories like the upcoming *James Webb Space Telescope* will require such data utilizing the best theoretical methods available.

#### 2. Computational details

Both QFFs require tight geometry optimizations. The CCSD(T)-F12/cc-pVTZ-F12 [35] (F12-TZ) QFF is simply a single optimization at this level, while the CcCR uses a CCSD(T)/aug-cc-pV(5+d) Z [36,37] geometry with the structural variables modified for inclusion of a shift in core electron correlation. This latter is done through CCSD(T) with the Martin-Taylor (MT) core electron correlating basis set [38] both including and excluding the core electrons in the optimizations. The differences in the variables are added to the CCSD(T)/aug-cc-pV5Z geometry. From either refer-

ence geometry of planar,  $C_s$  HAINP (Fig. 1A), the following coordinates are displaced to produce the QFF:

$$S_1(a') = r(H - AI) \tag{1}$$

 $S_2(a') = r(\mathrm{Al} - \mathrm{N}) \tag{2}$ 

$$S_3(a') = r(N - P) \tag{3}$$

$$S_4(a') = \angle (H - Al - N) \tag{4}$$

$$S_5(a') = \angle (Al - N - P) \tag{5}$$

$$S_6(a'') = \tau(H - Al - N - P). \tag{6}$$

 $S_1$  through  $S_3$  have 0.005 Å displacements while  $S_4$  through  $S_6$  have 0.005 radian displacements in line with previous, highly-accurate benchmarks for the same connectivities [39–41]. The F12-TZ QFF, naturally, requires this single level of theory at each of the 743 displaced, symmetry unique points. The CcCR requires: 1) CCSD(T)/a ug-cc-pV(T + d) Z, aug-cc-pV(Q+d) Z, and aug-cc-pV(5 + d) Z energies extrapolated via a 3-point formula [42] defined as

$$E(l) = A + B\left(l + \frac{1}{2}\right)^{-4} + C\left(l + \frac{1}{2}\right)^{-6};$$
(7)

2) CCSD(T)/MT with core and CCSD(T)/MT without core energies and the difference between them; and 3) the difference between CCSD(T)/cc-pVTZ-DK with and without the relativistic correction included.

The energies of both QFFs are gathered and fit in their respective surfaces via a least squares method with a sum of the residuals squared to less than  $10^{-16}$  a.u.<sup>2</sup> or better. The INTDER [43] program transforms the coordinates into Cartesian coordinates for generic inclusion into the SPECTRO program [44] where rotational and vibrational perturbation theory at second order (VPT2) [23,45,46] produces the spectroscopic constants and anharmonic fundamental vibrational frequencies, respectively. SPECTRO can treat Fermi resonances and even Fermi resonance polyads [47]. HAINP contains a  $2v_5 = 2v_6 = v_3 = v_4$  polyad so numbered with the sequence of vibrational frequencies discussed below; it also contains a  $v_6/v_5A$ -type Coriolis resonance. All electronic structure computations make use of MOLPRO 2015.1 [48,49] save for the MP2/augcc-pVDZ harmonic and anharmonic intensities in Gaussain16 [50,51].



Fig. 1. Depiction of the isomers for: (A) HAINP, (B) HAIPN, (C) HNAIP, and (D) HPAIN.

#### 3. Results and discussion

Four electronic states of HAINP all lie within 2000 cm<sup>-1</sup> of one another and compete to be the lowest energy state. The reason for the low-lying states arises from the nearly, but not perfectly, linear nature of the HAINP structure to begin with. The 1  ${}^{1}A'$  state's(core)  $(11a^{\prime 2})(12a^{\prime 2})(3a^{\prime \prime 2})(13a^{\prime 2})(14a^{\prime 2})(15a^{\prime 2})$  orbital occupation hides the fact that the 15*a*' orbital is actually only one-half of a n = 2particle-in-a-box  $\pi$  pair. The other half is the 4*a*" unoccupied molecular orbital that has a SCF/cc-pVTZ-F12 energy of -0.13 eV. Hence, the non-linearity of the  $\angle$ (Al–N–P) forces the  $\pi$  pair to split and doubly fill, in the 1  ${}^{1}A'$  state, the in-plane orbital of the otherwise degenerate orbital pair counter to Hund's rules. This creates easily accessible low-lying electronic states. If the equivalent orbitals are filled at the frontier with  $(15a'^1)(4a''^1)$ , the 1  ${}^{3}A''$  state (discussed in this work) is created. Doubly filling the 4a" orbital creates the 2  ${}^{1}A''$  state, and singly filling 16*a*' orbital, another low-lying  $\pi$ orbital, with an electron donated from the 15a' creates the 1  ${}^{3}A'$ state. Such behavior has been shown previously for similar perilinear organic molecules [52,53] and specifically with other, related aluminum bearing species such as AINS, AISO<sup>+</sup>, and AIPO [54-56].

Of the four, the 1  ${}^{1}A'$  and 1  ${}^{3}A''$  states described above are likely the lowest energy. Of the two, the 1  ${}^{3}A''$  state of HAINP is actually predicted to be lower in energy than the 1  ${}^{1}A'$ . However, adiabatic F12-TZ estimatations with anharmonic ZPVE inclusions put this value at less than 20 cm<sup>-1</sup>, specifically 19.6 cm<sup>-1</sup> or 0.06 kcal/mol at the very precision limit. The  $T_1$  diagnostic for the triplet is 0.028 and 0.036 for the singlet implying that the current or even more advanced methods short of full-CI, CBS limit, relativistic, coreelectron including computations likely cannot pin down which state is actually lower in energy, akin to the  ${}^{2}\Sigma^{+}/{}^{2}\Pi$  ground state debate from C<sub>4</sub>H [57]. As such, the rovibrational nature of both states will be discussed. The singlet is more likely to be observed via radioastronomy due to its larger dipole moment and will, thus, begin the discussion.

#### 3.1. 1 <sup>1</sup>A' HAINP

Counter to the strong bonding present between Al and O atoms and even Al—N bonds in model structures [9,8], the Al—N bond in HAINP is actually relatively weak at -18.62 kcal/mol from present F12-TZ harmonic zero-point vibrational energy (ZPVE) corrected computations. This is also carried through in the  $\sim 2.5$  mdyne/Å<sup>2</sup> force constant given in the supplemental information. While this bond is not egregiously weak, the fact that it is 17.7 % the strength of the Al—N bond in AlH<sub>2</sub>NH<sub>2</sub> implies a total change of bonding character [9]. Consequently, aluminum bonded to two atoms appears to have different properties than that bonded to three atoms. However, the N—P bond (with a force constant of  $\sim 8.5$ mdyne/Å<sup>2</sup>) is rather strong.

From Table 1, the ~ 1.60 Å Al—H bond length is already 0.15 Å longer than what most third-row atoms demonstrate for hydride bonds, but the Al—N length at 1.834 Å is closer to that typically expected (1.76 Å), if slightly longer [9]. The F12-TZ P=N bond length is 1.494 Å in the isolated PN diatomic, implying that the same bond in HAINP is somewhat perturbed. This is corroborated by the 150° Al—N—P bond angle. Even with many unexpected behaviors, this molecule still exhibits the preference for third-row atoms not to bond with one another [58].

The HAIPN isomer (Fig. 1B) lies 17.31 kcal/mol (from F12-TZ computations) above the HAINP but is a van der Waals complex between AlH and PN (with the phosphorus pointed at the hydrogen) with a complexation energy of 1.30 kcal/mol and a H—P bond length of 2.97 Å, the closest point between the two diatomic por-

Table 1	
The F12-TZ and CcCR Rotational Constants	(in MHz unless otherwise marked).

	1 <sup>1</sup> A' I	HAINP	1 <sup>3</sup> A" HAINP	
	F12-TZ	CcCR	F12-TZ	
$r_0(H-AI)$	1.59946	1.59599	1.59967	
$r_0(Al-N)$	1.83471	1.83429	1.78611	
$r_0(N-P)$	1.52861	1.52211	1.53563	
∠(H—Al—N)	108.383	106.775	117.094	
∠(Al—N—P)	159.481	159.480	173.920	
Ae	185526.4	182735.2	271297.9	
$B_e$	3084.4	3102.5	3059.4	
C <sub>e</sub>	3034.0	3050.7	3025.3	
$A_0$	186243.0	183187.4	275261.6	
$B_0$	3076.4	3093.0	3059.0	
C <sub>0</sub>	3024.3	3039.4	3022.9	
$A_1$	180818.5	177689.1	267607.3	
<i>B</i> <sub>1</sub>	3075.0	3090.9	3057.4	
<i>C</i> <sub>1</sub>	3021.6	3036.1	3020.6	
A <sub>2</sub>	182992.3	180317.6	275861.6	
B <sub>2</sub>	3060.1	3076.3	3041.3	
C <sub>2</sub>	3007.7	3022.6	3005.8	
A <sub>3</sub>	192715.8	188565.7	289767.1	
B <sub>3</sub>	3075.0	3091.6	3058.0	
C <sub>3</sub>	3021.7	3036.6	3020.2	
$A_4$	187999.1	185956.7	276799.7	
$B_4$	3059.7	3074.3	3052.3	
<i>C</i> <sub>4</sub>	3006.1	3019.4	3015.3	
A <sub>5</sub>	191730.4	187984.2	277455.9	
B <sub>5</sub>	3085.4	3101.8	3073.9	
C <sub>5</sub>	3029.4	3044.1	3033.0	
A <sub>6</sub>	182634.9	179515.4	272005.8	
$B_6$	3087.2	3103.6	3069.9	
C <sub>6</sub>	3040.3	3055.1	3038.0	
$\Delta_J$ (kHz)	0.591	0.611	0.445	
$\Delta_K$ (MHz)	112.138	100.900	97.030	
$\Delta_{JK}$ (MHz)	-0.090	-0.068	0.085	
$\delta_I$ (Hz)	19.124	18.834	5.590	
$\delta_K$ (kHz)	27.046	29.077	53.601	
$\Phi_J$ (mHz)	0.213	0.156	0.043	
$\Phi_{lK}$ (kHz)	94.671	75.336	16.225	
$\Phi_{Kl}$ (Hz)	-0.649	-0.643	0.333	
$\Phi_K$ (kHz)	152.637	154.228	-1.033	
$\phi_i$ (mHz)	0.061	0.059	0.061	
$\phi_{ik}$ (mHz)	-18.271	-24.547	236.206	
$\phi_{\nu}$ (kHz)	0.379	0.362	1.083	
$\mu$ (D) <sup>a</sup>		0.95	0.46	

 $^{\rm a}\,$  CCSD(T)/aug-cc-pV(5 + d) Z dipole moment at the 1  $^1A'$  HAINP CcCR equilibrium geometry and F12-TZ for 1  $^3A''$  HAINP.

tions. The HAIPN isomer's F12-TZ harmonic vibrational frequencies are closely aligned with the isolated diatomic AlH and PN molecules given in Table 2. The imaginary frequency corresponds to the in-plane heavy atom bending motion, but the HAIPN geometry uses exceptionally tight convergence criteria (a maximum step must be less than 10<sup>-8</sup>) like HAINP. Hence, the frequencies for this (and the other three, low frequency modes) should not be viewed as quantitative predictions but indicators of non-covalent interactions. Additionally, the linear HNAIP isomer (Fig. 1C) is computed to be 36.29 kcal/mol above bent HAINP, and the linear HPAIN isomer (Fig. 1D) is 42.20 kcal/mol above. These other two isomers may be of interest to future work, but the remainder of the present study will keep to the lowest energy isomer.

Returning to the titular molecule, HAINP, on the other hand, the two terminal stretching frequencies appear to be well-described between the two QFFs and are exhibiting notable intensities. The  $v_1$  Al—H stretch at 1763.2 cm<sup>-1</sup>, as given in Table 2, has an intensity of the level observed for inorganic oxides [58,59], much above what most organic molecules demonstrate. The  $v_2$  P—N stretch at 1261.6 cm<sup>-1</sup> is also bright at three-quarters that of the hydride stretch's intensity. MP2/aug-cc-pVDZ double harmonic intensities have been shown to corroborate higher-level computations quite

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	Coord. <sup>a</sup>			1 <sup>1</sup> A' HAINP		1 <sup>3</sup> A" H	AINP		
		Symm.	F12-TZ	CcCR	f	F12-FTZ	f	HAIPN <sup>b</sup>	Diatomic <sup>c</sup>
$\omega_1$	<i>S</i> <sub>1</sub>	<i>a</i> ′	1842.0	1841.1	547	1876.7	270	1667.6	1688.3
$\omega_2$	S <sub>3</sub>	a'	1285.4	1284.9	350	1314.9	1624	1353.6	1342.7
$\omega_3$	$S_4$	a'	517.3	516.0	123	581.8	73	125.7	
$\omega_4$	$S_2$	a'	462.7	481.3	72	524.8	80	59.0	
$\omega_5$	S <sub>5</sub>	a'	234.4	238.3	68	171.6	5	53.8i	
$\omega_6$	S <sub>6</sub>	<i>a</i> ″	148.5	153.0	0	156.8	14	81.8	
v <sub>1</sub>	$S_1$	a'	1761.6	1763.2	512	1813.1	211		
v <sub>2</sub>	S <sub>3</sub>	a'	1262.1	1261.6	379	1296.2	3662		
V3	$S_4$	<i>a</i> ′	503.6	513.8	80	604.8	2		
<i>v</i> <sub>4</sub>	$S_2$	<i>a</i> ′	455.8	456.0	37	529.8	125		
V5	S <sub>5</sub>	a'	235.4	237.8	78	166.7	5		
v <sub>6</sub>	S <sub>6</sub>	<i>a</i> ″	87.0	159.9	0	178.4 <sup>d</sup>	26		
70/0	-		2220.0	2220.2					

Table 2

The F12-TZ and CcCR OFF VPT2 Vibrational Frequencies (in  $cm^{-1}$ ) and MP2/aug-cc-pVDZ intensities (f in km/mol).

<sup>a</sup> Dominant coordinate (> 85% contributor).

<sup>b</sup> F12-TZ harmonic values. See text for discussion of imaginary frequency.

<sup>c</sup> F12-TZ harmonic values for AlH and NP, respectively.

<sup>d</sup> This reported frequency is set to the MP2/aug-cc-pVDZ result. Instability in the out-of-plane coordinate produces unphysical F12-TZ anharmonicites.

well [60,61], but this work also explores the anharmonic intensities at this same level of theory. There is little shift further implying that the less costly double-harmonics are well-behaved, semiquantitative predictors. In any case, the hydride stretching frequency is well above the diatomic, but the N—P is below implying that this molecule will exhibit clear deviations from its isolated diatomic constituents.

The other four HAINP vibrational frequencies reduce in both intensity and frequency as compared to  $v_1$  and  $v_2$ . The 513.8 cm<sup>-1</sup> CcCR  $v_3$  Al—N stretching frequency corroborates the weakened bonding between these two atoms previously discussed for the longer bond length and lower bond energy. Additionally, the  $v_6$  torsional motion is poorly described here by either QFF since F12-TZ is largely anharmonic, but CcCR is positively anharmonic. The near-prolate nature of the molecule and relatively weak Al—N bond likely both contribute to this disappointing behavior. Regardless, the comparison between F12-TZ and CcCR is actually exceptionally good in all cases except for  $v_6$ . The other modes agree between the two methods to 2.5 cm<sup>-1</sup> for the rest of the modes save  $v_3$  which only differs by 10.2 cm<sup>-1</sup> between 503.6 cm<sup>-1</sup> and 513.8 cm<sup>-1</sup>, respective of F12-TZ and CcCR.

The bottom portion of Table 1 gives the spectroscopic constants for HAINP including the rotational constants for the first fundamental of each mode (numbered in the same fashion as Table 2) and the quartic and sextic A-reduced Hamiltonian distortion constants. Even with its 108° and 159° bond angles, HAINP is clearly near-prolate with the *B* and *C* constants within 60 MHz of each other. Since CcCR is much more representative of experimentally-deduced rotational constants in the past [28], the CcCR *B*<sub>0</sub> and *C*<sub>0</sub> values of 3093.0 MHz and 3039.4 MHz should be utilized as the principle rotational constants. These give a *B*<sub>eff</sub> (defined as  $\frac{B_0-C_0}{2}$ ) of 3066.2 MHz. Additionally, 1 <sup>1</sup>*A*' HAINP exhibits a 0.95 D dipole moment which will make it rotationally-active.

## 3.2. 1 <sup>3</sup>A" HAINP

The spectral features of both these discussed singlet and triplet states will mix to some extent, but the dipole moment of  $1^{3}A''$  HAINP is 0.46 D, less than half that of  $1^{1}A'$  HAINP. Hence, the singlet will likely be a better candidate for unique radioastronomical detection. However, the equivalent CcCR  $1^{3}A''$  HAINP  $B_{eff}$  is 3056.8 MHz after taking the F12-TZ  $B_{eff}$  of 3041.0 MHz and adding 15.8 MHz, the difference in  $B_{eff}$  between CcCR and F12-TZ for the singlet state. This even more near-prolate form of HAINP will have

signal mirroring the 1  ${}^{1}A'$  state. Such a doubling could make for a clearer fingerprint for this molecule.

In the IR, 1  ${}^{3}A''$  HAINP gives indication of having brighter features making it more likely for detection in this region. Most notably, the  $v_2$  P—N stretch at 1296.2 cm<sup>-1</sup> has an exceptionally large intensity, and the  $v_1$  Al—H stretch at 1813.1 cm<sup>-1</sup> is also bright even if roughly half that of its singlet counterpart. Both of these anharmonic fundamentals are higher in frequency than those in the singlet state owing to the stronger bonding present in the two ends of the molecule in the 1  ${}^{3}A''$  state. The  $v_4$  Al—N stretch at 529.8 cm<sup>-1</sup> is also higher in frequency, and the  $v_6$  out-of-plane bend is, again, not well described by VPT2 with the F12-TZ QFF.

#### 4. Conclusions

Both the nearly-degenerate 1  ${}^{1}A'$  and 1  ${}^{3}A''$  states of HAINP have exceptionally-bright infrared transitions right in the heart of the mid-infrared. Unfortunately, both sets of the  $v_1$  and  $v_2$  bands fall in regions of astronomical spectra typically heavily populated with what are believed to be polycyclic aromatic hydrocarbons (PAHs) [62,63], specifically the C–C stretching as well as the bending regions in the 5.5  $\mu$ m to 9.0  $\mu$ m range. However, a potential rotational detection of HAINP through its singlet 0.95 D dipole moment and mirroring from the lower dipole 1  ${}^{3}A''$  state should allow for rigorous estimates of this molecule's abundance in any region. Consequently, some of the perceived PAH lines and infrared emission density in these spectral regions may actually arise from heavier *p*-block molecules even if in what are likely small numbers. Regardless, the presence of HAINP is possible in the atmospheres of metal-rich stars or cold clouds. It may serve as a reservoir of interstellar aluminum hydride and could facilitate subsequent phosphorus chemistry. The spectral data provided in this work are the necessary first step in understanding any such role this molecule may play in the chemistry of the larger universe.

#### **CRediT authorship contribution statement**

**Ryan C. Fortenberry:** Conceptualization, Methodology, Validation, Formal analysis, Resources, Data curation, Writing - original draft, Writing - review & editing, Visualization, Project administration, Funding acquisition. **Tarek Trabelsi:** Conceptualization, Software, Validation, Formal analysis, Investigation, Writing - review & editing. **Joseph S. Francisco:** Conceptualization, Methodology, Validation, Formal analysis, Writing - review & editing, Project administration.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Acknowledgements

RCF acknowledges funding from NASA Grant NNX17AH15G, NSF Grant OIA-1757220, and start-up funds provided by the University of Mississippi. Additionally, the authors acknowledge the wonderful body of work contributed to both the spectroscopy and astrochemistry communities by Prof. Schlemmer. He has been not only a titan of the field but also a gentleman-scientist, most notably.

#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jms.2021.111422.

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