


 Cite this: *Phys. Chem. Chem. Phys.*,
 2024, 26, 26363

Symmetry reduction induced by argon tagging gives access to low-lying excited states of FeH⁺ in the overtone region of the Fe–H stretching mode†

 Shan Jin,^{ib}^a Marcos Juanes,^{ib}^{ab} Christian van der Linde,^{ib}^a Milan Ončák^{ib}^{*a}
 and Martin K. Beyer^{ib}^{*a}

Iron is the most abundant transition metal in the interstellar medium (ISM), and is thought to be involved in a variety of astrochemical processes. Here, we present the infrared multiple photon dissociation (IRMPD) spectra of Ar_{1,2}FeH⁺ and their deuterated isotopologues in the region of 2240–14 000 cm⁻¹. The Fe–H overtone stretching mode in ArFeH⁺ and Ar₂FeH⁺ is observed at 3636 ± 28 cm⁻¹ and 3659 ± 13 cm⁻¹, respectively. Deuteration shifts these bands to 2618 ± 31 cm⁻¹ and 2650 ± 14 cm⁻¹ in ArFeD⁺ and Ar₂FeD⁺, respectively. Additionally, the spectra of Ar₂FeH⁺ and Ar₂FeD⁺ feature broad transitions at ~2200–4000 cm⁻¹ and ~4500–6500 cm⁻¹. We assign these bands to electronic transitions from the thermally populated X⁵A₂/X⁵A₁ ground state manifold into the A¹B₂ and B⁵A₁ states, which we model with multi-reference quantum chemical calculations including spin–orbit coupling. The calculations show that these transitions are symmetry forbidden in FeH⁺ and in the equilibrium geometry of ArFeH⁺/ArFeD⁺, while the zero-point oscillation of the bending mode of the triatomic molecule leads to some oscillator strength. Upon addition of the second argon atom, the transitions become weakly allowed in the equilibrium geometry of Ar₂FeH⁺/Ar₂FeD⁺ due to symmetry reduction from C_{∞v} to C_{2v}.

 Received 20th August 2024,
 Accepted 1st October 2024

DOI: 10.1039/d4cp03270e

rsc.li/pccp

Introduction

Iron is the most abundant transition metal on Earth, playing an important role in proteins and biochemistry in general.¹ It has also attracted attention in astrochemical research, in particular due to its abundance in the interstellar medium (ISM).^{2–7} Despite the high abundance of iron, the ISM detection of molecular species containing iron has so far been limited to FeO and FeCN.^{2,3} In the solar system, iron is present in planetary atmospheres as a meteoric ion, with FeH⁺ formation included in the models, *e.g.*, of the ionosphere of Jupiter.⁸ As outlined by E. Dwek⁹ and G. Bilalbegović *et al.*,¹⁰ iron is potentially a crucial element for understanding interstellar processes and the evolution of interstellar dust. The high abundance of iron in our galaxy together with its limited detection as neutral or ionized gas-phase atom in the ISM is commonly explained by the incorporation of iron in interstellar

dust.^{11–13} In support of these arguments, Westphal *et al.* as well as Corrales *et al.* recently reported that ISM X-ray absorption data closely match laboratory spectra of iron oxide/hydroxide minerals.^{14,15} However, although ISM observations show atomic iron to be severely depleted, the recent detection of FeCN in the ISM³ or the observed evidence for the presence of FeO in interstellar molecular clouds² shows that iron containing gas-phase molecular species are present in the ISM. Small molecules or complexes containing iron may thus contribute to the hidden iron budget. The previously proven presence of iron in the ISM together with the key role of transition metals in astrophysical environments^{16–19} call for more laboratory work on molecular transition metal compounds.

Since atomic iron is largely ionized in the ISM, and hydrogen is the by far most abundant element, the diatomic FeH⁺ molecular ion has been discussed as a potential iron reservoir species.²⁰ A series of quantum chemical studies focused on the electronic structure of FeH⁺ and predicted low-lying electronically excited states.^{20–22} As a first experimental characterization of FeH⁺, we recently studied the vibrational spectrum of Ar₂FeH⁺ in the 1600–2200 cm⁻¹ region.²³ The Fe–H stretching mode was observed at 1860 cm⁻¹, significantly blue-shifted by the argon tag from the 1810.4 cm⁻¹ calculated for bare FeH⁺ by Cheng and DeYonker.²⁰ Relatively intense combination bands

^a Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstraße 25, 6020 Innsbruck, Austria. E-mail: milan.oncak@uibk.ac.at, martin.beyer@uibk.ac.at

^b Departamento Química Física y Química Inorgánica, University of Valladolid, Paseo de Belén 7, 47011 Valladolid, Spain

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4cp03270e>





Fig. 2 Theoretical absorption cross-section calculation for the electronic transition of (a) ArFeH^+ and (b) Ar_2FeH^+ compared with the overtone of Fe–H/Fe–D vibrational stretching mode. For ArFeH^+ , structure sampling with only stretch vibrations (“2 vibrations”) and all frequencies (“4 vibrations”) were used, see text. Calculations were performed at the MRCI(8,7)+SO/aug-cc-pVQZ level of theory employing reflection principle modelling, with anharmonic overtone frequencies (shown in purple and red) at the B3LYP-D3/aug-cc-pVDZ level, broadened by Gaussians with the FWHM of 40 cm^{-1} .

by including the bending modes in the modeling (“4 vibrations”), a second band appears at approximately 2000 cm^{-1} with cross section below 10^{-21} cm^2 . As the bending vibrations are strongly anharmonic, the actual spectrum is probably even broader.

In Ar_2FeH^+ , Fig. 2b, the $X^5A_2/X'^5A_1 \rightarrow A^5B_1$ band at 1300 cm^{-1} has virtually the same structure as in ArFeH^+ . Two additional bands appear in the experimentally studied range due to the lower symmetry. Their intensity is considerably higher compared to the second band in ArFeH^+ . The broad bands centered at 2635 cm^{-1} and 3088 cm^{-1} for Ar_2FeH^+ in Fig. 1c can be assigned to the $X^5A_2/X'^5A_1 \rightarrow A'^5B_2$ transitions. The corresponding bands for Ar_2FeD^+ are observed at 2483 cm^{-1} and 3038 cm^{-1} , respectively. However, no significant change in the structure of the electronic spectrum was observed for the deuterated species.

The cross sections for the electronic absorption in the simulated Ar_2FeH^+ and Ar_2FeD^+ spectra, Fig. 2b, are very similar to the values calculated for the Fe–H/D overtone transitions $\nu = 0 \rightarrow 2$, consistent with the experimental spectra shown in Fig. 1c and d. In Fig. 2a, the weak broad bands emerging due to breaking of the linearity of $\text{ArFeH}^+/\text{ArFeD}^+$ may explain the unspecific background observed experimentally. Our results thus experimentally confirm the predictions of low-lying electronic states in FeH^+ by Sodupe *et al.*, Langhoff *et al.* and Cheng and DeYonker.^{20–22}

The additional band in the electronic spectrum of Ar_2FeH^+ predicted beyond 4000 cm^{-1} , $X'^5A_1 \rightarrow B^5A_1$, lies outside the range covered by Fig. 1. To validate the prediction, we performed further spectral measurements up to 14000 cm^{-1} , see Fig. 3 and Fig. S4 (ESI[†]). The predicted band is indeed there, with a cross section close to the value predicted in Fig. 2. While the main band is predicted by theory at $3500\text{--}5000\text{ cm}^{-1}$, we observe it shifted to the blue by about 1000 cm^{-1} (0.12 eV), within the expected accuracy of the electronically excited state



Fig. 3 Experimental spectrum of the electronic transition $B \leftarrow X'$ of Ar_2FeH^+ in the $4450\text{--}7000\text{ cm}^{-1}$ range.

calculations. With the reduced symmetry in Ar_2FeH^+ , transitions to low-lying electronically excited states thus become spectroscopically accessible.

Conclusion

In this study, we present a detailed theoretical and experimental investigation on the vibrational overtone transition of argon-tagged FeH^+ and FeD^+ and electronic transitions to low-lying excited states using IRMPD spectroscopy coupled with high-level quantum chemical calculations. We observed the overtone transition ($\nu = 0 \rightarrow 2$) of Fe–H stretching in Ar_2FeH^+ , ArFeH^+ , and their deuterated isotopologues. According to the comparison between experiment and theory, the Fe–H fundamental stretching and its first overtone in bare FeH^+ is expected in the $1790\text{--}1840\text{ cm}^{-1}$ and $3525\text{--}3619\text{ cm}^{-1}$ region, respectively.

Electronic transitions to the low-lying $B^5\Sigma^+$ state in FeH^+ are symmetry forbidden. The second argon atom permanently reduces the $C_{\infty v}$ symmetry of FeH^+ and ArFeH^+ to C_{2v} in Ar_2FeH^+ . This enhances the intensity of the transitions to low-lying excited states to about 10^{-20} cm^2 , making them fully accessible for IRMPD spectroscopy.

Data availability

The data supporting this article have been included as part of the ESI.[†]

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This research was funded in part by the Austrian Science Fund (FWF), Grant DOIs 10.55776/W1259 (DK-ALM, SJ, MKB) and 10.55776/P35013 (MO). The tunable OPO system is part of the Innsbruck Laser Core Facility, financed by the Austrian Federal Ministry of Education, Science and Research. The computational results presented have been obtained using the HPC infrastructure LEO of the University of Innsbruck. MJ thanks the Ministerio de Universidades of Spain and the Universidad de Valladolid (UVA) for a “Margarita Salas” postdoctoral contract (CONREC-2021-265). The isotope used in this research was



supplied by the U.S. Department of Energy Isotope Program, managed by the Office of Isotope R&D and Production.

References

- 1 P. A. Frey and C. E. Outten, *Curr. Opin. Chem. Biol.*, 2011, **15**, 257.
- 2 C. M. Walmsley, R. Bachiller, G. P. Des Forêts and P. Schilke, *Astrophys. J.*, 2002, **566**, L109–L112.
- 3 L. N. Zack, D. T. Halfen and L. M. Ziurys, *Astrophys. J. Lett.*, 2011, **733**, L36.
- 4 S. Zhukovska, T. Henning and C. Dobbs, *Astrophys. J.*, 2018, **857**, 94.
- 5 P. Tarakeshwar, P. R. Buseck and F. X. Timmes, *Astrophys. J.*, 2019, **879**, 1.
- 6 M. Fioroni, *Comput. Theor. Chem.*, 2016, **1084**, 196.
- 7 M. Fioroni, *Phys. Chem. Chem. Phys.*, 2014, **16**, 24312.
- 8 Y. Kim, *Icarus*, 2001, **150**, 261.
- 9 E. Dwek, *Astrophys. J.*, 2016, 825.
- 10 G. Bilalbegović, A. Maksimović and V. Mohaček-Grošev, *Mon. Not. R. Astron. Soc. Lett.*, 2017, **466**, L14–L18.
- 11 B. D. Savage and R. C. Bohlin, *Astrophys. J.*, 1979, **229**, 136.
- 12 E. B. Jenkins, *Astrophys. J.*, 2009, **700**, 1299.
- 13 G. Delgado-Inglada, M. Rodríguez, A. Mampaso and K. Viironen, *Astrophys. J.*, 2009, **694**, 1335.
- 14 L. Corrales, E. V. Gotthelf, E. Gattuzi, T. R. Kallman, J. C. Lee, M. Martins, F. Paerels, I. Psaradaki, S. Schippers and D. W. Savin, *Astrophys. J.*, 2024, **965**, 172.
- 15 A. J. Westphal, A. L. Butterworth, J. A. Tomsick and Z. Gainsforth, *Astrophys. J.*, 2019, **872**, 66.
- 16 G. Serra, B. Chaudret, Y. Saillard, A. Le Beuze, H. Rabaa, I. Ristorcelli and A. Klotz, *Astron. Astrophys.*, 1992, **260**, 489.
- 17 W. W. Duley, *Astrophys. J.*, 1979, **227**, 824.
- 18 K. Nomoto, C. Kobayashi and N. Tominaga, *Annu. Rev. Astron. Astrophys.*, 2013, **51**, 457.
- 19 K. Lodders, *Astrophys. J.*, 2003, **591**, 1220.
- 20 Q. Cheng and N. J. DeYonker, *J. Chem. Phys.*, 2019, **150**, 234304.
- 21 M. Sodupe, J. M. Lluch, A. Oliva, F. Illas and J. Rubio, *J. Chem. Phys.*, 1989, **90**, 6436.
- 22 S. R. Langhoff and C. W. Bauschlicher, *Astrophys. J.*, 1991, **375**, 843.
- 23 S. Jin, J. Heller, C. van der Linde, M. Ončák and M. K. Beyer, *J. Phys. Chem. Lett.*, 2022, **13**, 5867.
- 24 M. Herman, T. Földes, K. Didriche, C. Lauzin and T. Vanfleteren, *Int. Rev. Phys. Chem.*, 2016, **35**, 243.
- 25 J. Kozubal, T. R. Heck and R. B. Metz, *J. Phys. Chem. A*, 2019, **123**, 4929.
- 26 D. A. Wild, K. T. Kuwata, C.-K. Wong, J. D. Lobo, A. Deev, T. S. Schindler, M. Okumura and E. J. Bieske, *J. Phys. Chem. A*, 2010, **114**, 4762.
- 27 J. Jin, T. Wulf, M. Jorewitz, T. Heine and K. R. Asmis, *Phys. Chem. Chem. Phys.*, 2023, **25**, 5262.
- 28 T. C. Cheng, B. Bandyopadhyay, Y. Wang, S. Carter, B. J. Braams, J. M. Bowman and M. A. Duncan, *J. Phys. Chem. Lett.*, 2010, **1**, 758.
- 29 T. C. Cheng, L. Jiang, K. R. Asmis, Y. Wang, J. M. Bowman, A. M. Ricks and M. A. Duncan, *J. Phys. Chem. Lett.*, 2012, **3**, 3160.
- 30 R. V. Olkhov, S. A. Nizkorodov and O. Dopfer, *J. Chem. Phys.*, 1998, **108**, 10046.
- 31 R. F. Höckendorf, O. P. Balaj, C. van der Linde and M. K. Beyer, *Phys. Chem. Chem. Phys.*, 2010, **12**, 3772.
- 32 C. Berg, T. Schindler, G. Niedner-Schatteburg and V. E. Bondybey, *J. Chem. Phys.*, 1995, **102**, 4870.
- 33 V. E. Bondybey and J. H. English, *J. Chem. Phys.*, 1981, **74**, 6978.
- 34 T. G. Dietz, M. A. Duncan, D. E. Powers and R. E. Smalley, *J. Chem. Phys.*, 1981, **74**, 6511.
- 35 M. A. Duncan, *Rev. Sci. Instrum.*, 2012, **83**, 41101.
- 36 A. G. Marshall, C. L. Hendrickson and G. S. Jackson, *Mass Spectrom. Rev.*, 1998, **17**, 1.
- 37 O. P. Balaj, C. B. Berg, S. J. Reitmeier, V. E. Bondybey and M. K. Beyer, *Int. J. Mass Spectrom.*, 2009, **279**, 5.
- 38 R. C. Dunbar, *Mass Spectrom. Rev.*, 2004, **23**, 127.
- 39 R. C. Dunbar, *J. Phys. Chem.*, 1994, **98**, 8705.
- 40 P. D. Schnier, W. D. Price, R. A. Jockusch and E. R. Williams, *J. Am. Chem. Soc.*, 1996, **118**, 7178.
- 41 T. Schindler, C. Berg, G. Niedner-Schatteburg and V. E. Bondybey, *Chem. Phys. Lett.*, 1996, **250**, 301.
- 42 B. S. Fox, M. K. Beyer and V. E. Bondybey, *J. Phys. Chem. A*, 2001, **105**, 6386.
- 43 D. Thölmann, D. S. Tonner and T. B. McMahon, *J. Phys. Chem.*, 1994, **98**, 2002.
- 44 M. Salzburger, M. Ončák, C. van der Linde and M. K. Beyer, *J. Am. Chem. Soc.*, 2022, **144**, 21485.
- 45 A. Herburger, C. van der Linde and M. K. Beyer, *Phys. Chem. Chem. Phys.*, 2017, **19**, 10786.
- 46 A. Herburger, M. Ončák, C.-K. Siu, E. G. Demissie, J. Heller, W. K. Tang and M. K. Beyer, *Chem. – Eur. J.*, 2019, **25**, 10165.
- 47 J. Heller, M. Ončák, N. K. Bersenkovitsch, C. van der Linde and M. K. Beyer, *Eur. J. Mass Spectrom.*, 2019, **25**, 122.
- 48 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16 Revision A.03*, 2016.
- 49 A. Nicklass, M. Dolg, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1995, **102**, 8942.



- 50 S. Y. Lee, R. C. Brown and E. J. Heller, *J. Phys. Chem.*, 1983, **87**, 2045.
- 51 M. K. Prakash, J. D. Weibel and R. A. Marcus, *J. Geophys. Res.-Atmos.*, 2005, **110**, 380.
- 52 M. Ončák, L. Šišťík and P. Slavíček, *J. Chem. Phys.*, 2010, **133**, 174303.
- 53 H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby and M. Schütz, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2012, **2**, 242.
- 54 H.-J. Werner, P. J. Knowles, F. R. Manby, J. A. Black, K. Doll, A. Heßelmann, D. Kats, A. Köhn, T. Korona, D. A. Kreplin, Q. Ma, T. F. Miller, A. Mitrushchenkov, K. A. Peterson, I. Polyak, G. Rauhut and M. Sibaev, *J. Chem. Phys.*, 2020, **152**, 144107.
- 55 C. M. Western, *J. Quant. Spectrosc. Radiat. Transf.*, 2017, **186**, 221.
- 56 M. Hütter, G. Schöpfer, M. Salzburger, M. K. Beyer and M. Ončák, *RSC Adv.*, 2024, **14**, 22185.
- 57 M. Salzburger, M. Hütter, C. van der Linde, M. Ončák and M. K. Beyer, *J. Chem. Phys.*, 2024, **160**, 134304.

