Note

High-precision *R*-branch transition frequencies in the v_2 fundamental band of H_3^+

CrossMark

Adam J. Perry [a], James N. Hodges [a], Charles R. Markus [a], G. Stephen Kocheril [a], Benjamin J. McCall [a,b,*]

[a] *Department of Chemistry, University of Illinois, Urbana, IL 61801, USA*
[b] *Department of Astronomy, University of Illinois, Urbana, IL 61801, USA*

ABSTRACT

The H_3^+ molecular ion has served as a long-standing benchmark for state-of-the-art *ab initio* calculations of molecular potentials and variational calculations of rovibrational energy levels. However, the accuracy of such calculations would not have been confirmed if not for the wealth of spectroscopic data that has been made available for this molecule. Recently, a new high-precision ion spectroscopy technique was demonstrated by Hodges et al., which led to the first highly accurate and precise ($\sim$MHz) H_3^+ transition frequencies. As an extension of this work, we present ten additional *R*-branch transitions measured to similar precision as a next step toward the ultimate goal of producing a comprehensive high-precision survey of this molecule, from which rovibrational energy levels can be calculated.

© 2015 Elsevier Inc. All rights reserved.

As the simplest polyatomic molecule, H_3^+ serves as an important benchmark system for *ab initio* calculation of molecular potential energy surfaces (PES) and spectra. The degree to which state-of-the-art calculations of the rovibrational transitions agree with experimental measurements is impressive, and is approaching the limit of the experimental uncertainty, typically on the order of 150–300 MHz (for a thorough review on previous laboratory spectroscopy of H_3^+ see Ref. [1]). Recent calculations [2] based on the highly accurate Born–Oppenheimer PES of Pavanello et al. [3], which included diagonal Born–Oppenheimer corrections (*i.e.* the adiabatic correction) and relativistic corrections, reproduce all known rovibrational energy levels for all isotopologues within 0.2 cm^{-1}. Shortly thereafter, Diniz et al. [4] developed a method for approximating the non-adiabatic effects using a "core-mass" approach whereby the nuclei are given coordinate-dependent masses as they undergo vibrational motion. Comparison to twelve high-precision ($\sim$10 MHz) transitions arising from low-lying rovibrational energy levels yields an agreement between experiment and theory of $\sim$0.001 cm^{-1} ($\sim$30 MHz). Beyond these calculations Lodi and co-workers [5] have developed the first quantum electrodynamic correction surface for H_3^+, which demonstrated the importance of including these effects, as well as the need for a more complete model for taking into account non-adiabatic effects.

Since the accuracy of theoretical calculations is now reaching the level of the experimental uncertainty, improved spectroscopic measurements are needed in order to push the bounds of theoretical calculations. In this note we present ten new high-precision spectroscopic measurements in the v_2 fundamental band of H_3^+. These new frequencies, combined with those measured by Hodges et al. [6], represent a step towards completing a thorough high-precision spectroscopic survey for this important fundamental species. The spectra were acquired using the technique Noise-Immune Cavity Enhanced Optical Heterodyne Velocity Modulation Spectroscopy (NICE-OHVMS), in which traditional velocity modulation spectroscopy [7] is augmented with cavity enhancement and heterodyne modulation [8]. The instrument (described in detail in [6,9]) utilizes a high-power, continuous wave, optical parametric oscillator whose idler beam is coupled into an external optical cavity which surrounds a water-cooled AC positive column discharge of H_2 gas. Inside the cell, the pressure is maintained at 300–400 mTorr and the discharge is driven at frequencies of 40–50 kHz. Light transmitted through the cavity is detected by a fast photodiode detector whose signal is demodulated first at the heterodyne frequency ($\sim$80 MHz) by a pair of electronic mixers and then again at twice the discharge frequency (80–100 kHz) by a pair of lock-in amplifiers. This detection scheme results in four channels of detection, producing signals from each heterodyne mixer that are in-phase and 90° out of phase (in quadrature) with the sinusoidal driving voltage of the discharge. Frequency calibration of the spectra is accomplished by measuring the difference in frequency between the pump and signal waves. Measurements of these beams are obtained with a near-infrared wavelength meter and optical frequency comb.

* Corresponding author at: Department of Chemistry, University of Illinois, Urbana, IL 61801, USA.

Due to the bi-directional nature and optical power enhancement of the external optical cavity, it is possible to perform sub-Doppler spectroscopy which enables high-precision line center measurements. Such a spectrum is illustrated in Fig. 1. Line centers are extracted via a simultaneous fit of all four detection channels to the sub-Doppler features. In the fit the line center, heterodyne detection angle, and full-width of the feature are all shared parameters between the four channels. Previous high-precision measurements were limited to transitions from lower-J levels and these new measurements have expanded the range up to $J = 6$. All newly measured transition frequencies are reported in Table 1. Uncertainties in the line centers are assigned as the standard deviation of a data set composed of at least five scans for each transition, and as a result are highly dependent on the signal-to-noise ratio of the sub-Doppler features. The precision to which these lines have been measured represents an improvement over previous measurements of two orders of magnitude for most of the transitions. It is worth noting that the works of Oka [10], and Lindsay et al. [1] appear to be highly accurate, and their claimed uncertainties may be a bit conservative.

The only new measurement that falls outside of the stated uncertainties of the previous work is that of $R(3,3)^u$, for which we record a frequency that is 15 MHz lower than that reported by Wu et al. [11]. Though this discrepancy is not completely unreasonable (1.5σ), we set out to confirm this frequency by performing a second, independent measurement of this transition. Doing so yielded the same value (to within our specified uncertainty). To eliminate any possibility of an unexpected systematic error in our frequency calibration, we immediately remeasured the $R(1,0)$ transition, which was in good agreement with Hodges et al. and Wu et al., and we still obtain the same value for its line center. These tests leave us confident in the accuracy of our $R(3,3)^u$ measurement.

Table 1
Newly measured rovibrational transitions in the ν_2 fundamental band of H_3^+ and a comparison to previous values. All units are in MHz.

| Transition[a]	This work	Previous	Diff.
$R(4,3)^l$	86778433.66(76)	86778225(300)[b]	208.66
$R(3,3)^u$	87480191.43(117)	87480207(10)[c]	−15.57
$R(3,2)^u$	87640201.59(254)	87640158(300)[b]	43.59
$R(3,1)^u$	87789812.71(130)	87789754(300)[b]	58.71
$R(3,0)$	87844195.67(122)	87844077(300)[b]	118.67
$R(5,5)^l$	88620962.34(144)	88620809(300)[b]	153.34
$R(6,6)^l$	90368280.18(102)	90368359(150)[d]	−78.82
$R(4,3)^u$	90394720.09(232)	90394651(150)[d]	69.09
$R(4,2)^u$	90673895.29(179)	90673968(300)[d]	−72.71
$R(4,1)^u$	90831978.56(177)	90832078(150)[d]	−99.44

[a] Labels for these transitions refer to (J, G); for more details on H_3^+ notation see [1].
[b] Ref. [10].
[c] Ref. [11].
[d] Ref. [12].

Work is now underway to extend the frequency coverage of the spectrometer which will allow us to measure P and Q branch transitions in this band. Once this is accomplished it will be possible to begin measuring energy level spacings in the ground vibrational state with precision that has never before been achieved. Upon completion of the fundamental band measurements, a survey of transitions in the $2\nu_2^{\ell=2} \leftarrow \nu_2$ hot band along with transitions in the first overtone band ($2\nu_2^{\ell=2} \leftarrow 0$) will allow us to determine relative energy spacings among levels within the *ortho* and *para* species. Finally, a fit of the ground state energy levels to a modified Watson-type Hamiltonian will allow for absolute energy levels to be extracted. Once completed this work will equip theorists with a complete and highly precise list of experimentally determined
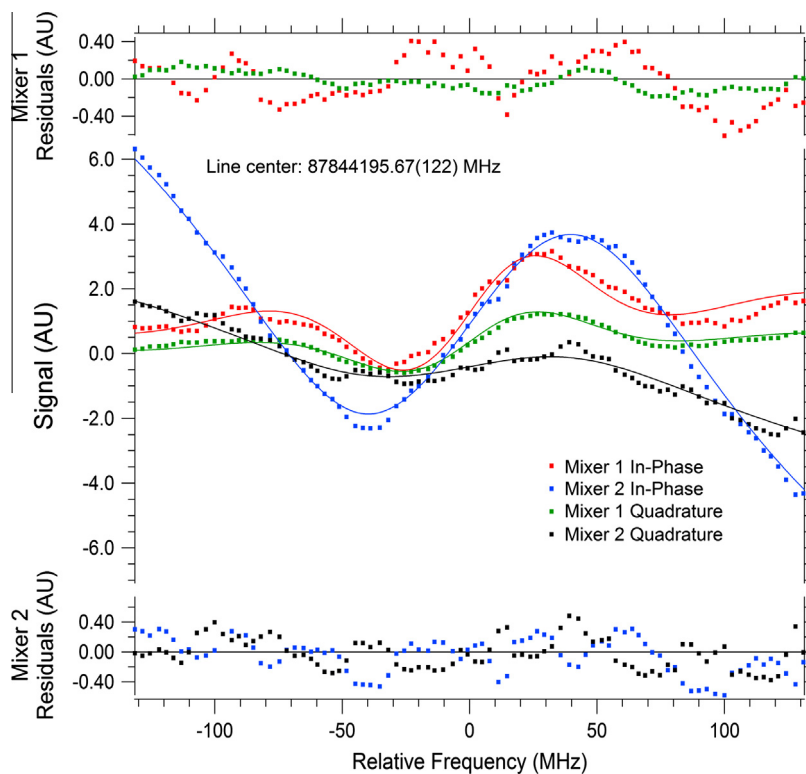
Fig. 1. A NICE-OHVMS scan of sub-Doppler feature of the $R(3,0)$ fundamental band transition of H_3^+ centered at 87844195.67(122) MHz. Signals from each of the four detection channels are shown (dots) and are fitted simultaneously (solid traces) with the line center as a shared parameter. The odd symmetry of the line shapes is a result of the applied modulation scheme.

rovibrational energy levels for this critically important molecular system.

Acknowledgments

References

[1] C. Lindsay, B.J. McCall, J. Mol. Spectrosc. 210 (2001) 60–83.
[2] O.L. Polyansky, A. Alijah, N.F. Zobov, I.I. Mizus, R.I. Ovsyannikov, J. Tennyson, L. Lodi, T. Szidarovszky, A.G. Császár, Philos. Trans. A Math. Phys. Eng. Sci. 370 (2012) 5014–5027.
[3] M. Pavanello, L. Adamowicz, A. Alijah, N.F. Zobov, I.I. Mizus, O.L. Polyansky, J. Tennyson, T. Szidarovszky, A.G. Császár, J. Chem. Phys. 136 (2012) 184303.
[4] L.G. Diniz, J.R. Mohallem, A. Alijah, M. Pavanello, L. Adamowicz, O.L. Polyansky, J. Tennyson, Phys. Rev. A 88 (2013) 032506.
[5] L. Lodi, O.L. Polyansky, J. Tennyson, A. Alijah, N.F. Zobov, Phys. Rev. A 89 (2014) 032505.
[6] J.N. Hodges, A.J. Perry, P.A. Jenkins II, B.M. Siller, B.J. McCall, J. Chem. Phys. 139 (2013) 164201.
[7] C. Gudeman, M. Begemann, J. Pfaff, R. Saykally, Phys. Rev. Lett. 50 (1983) 727–731.
[8] B.M. Siller, M.W. Porambo, A.A. Mills, B.J. McCall, Opt. Express 19 (2011) 24822–24827.
[9] K.N. Crabtree, J.N. Hodges, B.M. Siller, A.J. Perry, J.E. Kelly, P.A. Jenkins II, B.J. McCall, Chem. Phys. Lett. 551 (2012) 1–6.
[10] T. Oka, Philos. Trans. R. Soc. A 303 (1981) 543–549.
[11] K.-Y. Wu, Y.-H. Lien, C.-C. Liao, Y.-R. Lin, J.-T. Shy, Phys. Rev. A 88 (2013) 032507.
[12] C. Lindsay, R.M. Rade, T. Oka, J. Mol. Spectrosc. 210 (2001) 51–59.