

Do H_5^+ and Its Isotopologues Have Rotational Spectra?

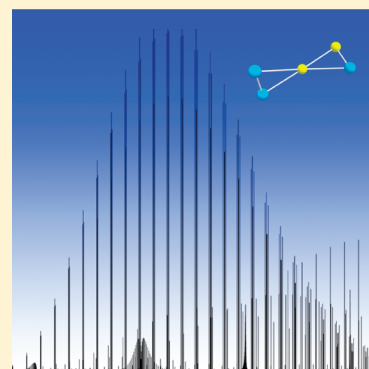
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S Supporting Information

ABSTRACT: High-level ab initio calculations predict a C_{2v} equilibrium geometry and large permanent dipole for H_5^+ , whereas rigorous Diffusion Monte Carlo calculations on a global potential surface show a completely symmetric zero-point averaged D_{2d} structure for H_5^+ , HD_4^+ , and D_5^+ , resulting in no permanent dipole moment. This dramatic departure from the conventional molecular structure is due to the highly fluxional nature of this cation. For the isotopologues H_4D^+ , H_3D_2^+ , and H_2D_3^+ , we predict nonzero dipole moments in the ground vibrational state and present corresponding simulated rotational spectra up to 3 THz. These predictions can guide the laboratory studies necessary for observational searches.

SECTION: Molecular Structure, Quantum Chemistry, General Theory



H_5^+ and CH_5^+ have been shown in full-dimensional quantum calculations to be highly fluxional cations, even in the ground vibrational state. Both cations have attracted general interest owing to this unusual fluxionality, which defies the conventional chemical picture of a structure being given by an equilibrium structure.^{1–5} In addition, both cations are highly likely to be present and influential in the chemistry of the interstellar medium,^{6–8} but neither has been detected, in large part because the high-resolution rotational spectra required for their definitive detections are unknown.

Consider H_5^+ and its deuterated analogs, which are the subject of this Letter. Low-resolution vibrational spectra have recently been reported and correctly interpreted for H_5^+ and D_5^+ in joint experimental–theoretical work⁹ that built on the pioneering early work of Okumura and Lee;¹⁰ however, no experimental spectra have been reported for mixed isotopologues. Experimental vibrational spectra have been reported above the lowest dissociation threshold energy for H_5^+ (refs 9 and 10) and D_5^+ (ref 9). In the most recent work,⁹ calculated spectra were in good agreement with experiment. The theoretical work made use of full-dimensional potential energy¹¹ and dipole moment surfaces⁹ with a proper delocalized description of the central proton to obtain the IR absorption spectrum of H_5^+ and D_5^+ . In that work (and previous full-dimensional calculations), the zero-point (ZP) averaged structures of these cations were shown to be highly symmetric, with the proton equally shared between the H_2 (D_2) groups. This contrasts sharply with the equilibrium structure of H_5^+ , which is of C_{2v} symmetry¹¹ and which can be characterized as H_3^+-H_2 .

This difference between the equilibrium and zero-point averaged structures raises the question of whether these cations have permanent electric dipole moments and hence pure rotational spectra. The dipole moment for H_5^+ at the C_{2v} structure is trivial to calculate; we obtain a magnitude of 1.75 D from the recent dipole moment surface.¹¹ However, it is

immediately clear that the dipole moment of the ZP-averaged structure is zero for the symmetric ions H_5^+ , D_5^+ , and HD_4^+ .

For the mixed isotopologues of these cations, the results are more nuanced, and, in fact, for some species, we predict nonzero, ZP-averaged dipole moments. We report those results here along with predictions of the associated rotational spectra at two temperatures. Specifically, we predict rotational spectra for H_2D_3^+ , H_3D_2^+ , and H_4D^+ at a level of accuracy that provides useful guides to laboratory-based searches for these species.

The present theoretical work relies heavily on the recent work of Acioli et al., who reported unbiased and importance sampling quantum Diffusion Monte Carlo (DMC) calculations of the ZP energies and ZP-averaged state structures¹² of H_5^+ , H_4D^+ , H_3D_2^+ , H_2D_3^+ , HD_4^+ , and D_5^+ using a very accurate ab initio potential energy surface.¹¹ Results from the two sets of DMC calculations agree very well with each other. The key results of those calculations are summarized in Figure 1, which shows the ZP-averaged structures for the lowest energy isotopomers of the three isotopologues with nonzero dipole moments, H_4D^+ , H_3D_2^+ , and H_2D_3^+ . The rotational constants and dipole moment components along the principal axes are given in Table 1. (Note that from the Acioli et al. calculations,¹² there is a higher-energy isotopomer of HD_4^+ that lies 44 cm^{-1} in energy above the isotopomer considered here. This isotopomer would also have a nonzero dipole moment, but we do not include it in the present analysis.)

The rotational spectrum for each isotopologue having a permanent dipole moment (H_2D_3^+ , H_3D_2^+ , and H_4D^+) was predicted up to 3 THz at rotational temperatures of $T_{\text{rot}} = 20$ and 300 K using the CALPGM suite of programs developed by Pickett and coworkers.¹³ The predictions were performed using

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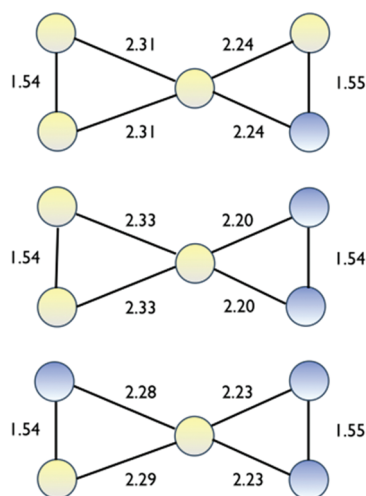


Figure 1. ZP-averaged structures and bond lengths for H_4D^+ (top), H_3D_2^+ (middle), and H_2D_3^+ (bottom). Deuterium atoms are indicated by a blue shade.

the rotational constants and dipole moments given in Table 1. A standard asymmetric top Hamiltonian in the I^r -representation was used for these predictions. The resulting spectra are shown in Figure 2. Full spectral catalogs in the CALPGM format are available for each species at 300 K in the Supporting Information.

The predicted pure rotational spectra are quite rich, with H_3D_2^+ and H_4D^+ displaying a - and b -type rotational spectral patterns and H_2D_3^+ displaying a - and c -type patterns. The intensities predicted for the pure rotational transitions are weak because of the small magnitudes of the dipole moments (in all cases ≤ 0.2 D). In addition, the spectral simulations presented in Figure 2 show that the most intense rotational transitions for these species arise in the far-IR, which is a notoriously difficult region for the spectroscopic study of ions. This presents a serious challenge for laboratory observation of these species because spectroscopic techniques in this frequency range are only now reaching the necessary levels of sensitivity to study a fluxional ion such as H_5^+ . The hydrogen-rich nature of the plasmas in which H_5^+ is most readily produced, however, offers the benefit of relatively high abundances. It has recently been demonstrated by McCall and coworkers that H_5^+ can be produced in relatively high abundance in a hollow cathode discharge cell.¹⁵ However, such methods typically produce ions at high temperatures. As is illustrated by Figure 2, a higher rotational temperature greatly increases the partition function, increasing spectral complexity while decreasing peak intensity. A supersonic expansion discharge source can cool these ions to a few tens of Kelvin. Simulations at 20 K show significantly reduced spectral complexity at these low temperatures and more than an order of magnitude enhancement in peak intensity at the lower frequencies that are accessible by existing millimeter-range laboratory spectroscopic techniques.

The high-level theoretical studies that this work draws upon provide insight into the dynamics of these highly fluxional systems. The most notable result here is that the minimum energy geometry for all deuterated isotopologues is the most symmetric structure, with a hydrogen atom as the central atom.

The spectral simulations presented here are intended as rough guides to experiment and not as quantitative predictions because the semirigid treatment of the zero-point averaged structure does not take into account the torsional motion of the “outer” two

Table 1. Rotational Constants and Dipole Moments for H_5^+ , H_4D^+ , H_3D_2^+ , H_2D_3^+ , HD_4^+ , and D_5^+

species	A (GHz)	B (GHz)	C (GHz)	μ_a (D)	μ_b (D)	μ_c (D)
H_5^+	748.0	92.0	92.0	0.00	0.00	0.00
H_4D^+	641.3	77.0	75.5	0.12	−0.04	0.00
H_3D_2^+	503.7	69.6	66.6	−0.20	0.00	0.00
H_2D_3^+	456.0	54.9	53.7	−0.09	0.00	−0.04
HD_4^+	381.9	48.0	48.0	0.00	0.00	0.00
D_5^+	381.9	47.1	47.1	0.00	0.00	0.00

diatomic moieties. We expect the first excited torsional bands for these isotopologues to fall somewhere between those calculated in previous work⁹ for H_5^+ and D_5^+ at ~ 80 and ~ 32 cm^{-1} , respectively. Spectral perturbations are expected to arise from the torsion-rotation coupling with these low-energy torsional bands. The perturbations are expected to be greatest in the 1 to 2.5 THz range, where the best energy match occurs between the pure rotational lines and the torsional bands. This will lead to increased spectral complexity in this range. Furthermore, given that the barrier to the internal motion is only ~ 160 cm^{-1} ,^{9,11} the pure rotational lines will be split into multiplets corresponding to each internal rotor state. Additional fine structure may occur from a tunneling process describing the exchange of the central atom by one of the atoms in the two diatom units. The combination of these factors will therefore significantly increase the spectral complexity beyond that shown in Figure 2. Still, the predictions shown in Figure 2 provide reasonable first estimates of the spectral windows within which initial laboratory searches for the pure rotational transitions of the H_5^+ mixed isotopologues should be conducted.

The results presented here show great promise for the possibility of detecting these fundamental ions in the interstellar medium once the laboratory spectrum is observed. Although the possible mechanisms for ionic cluster formation in interstellar environments are not well understood, given the high abundances and widespread distributions of the precursors H_2 and H_3^+ , H_5^+ and its isotopologues are plausible candidates for detection once laboratory spectra are available. The two temperatures shown in Figure 2 represent the two extremes of rotational temperatures typically displayed by molecules detected in interstellar clouds. The Boltzmann peaks for these isotopologues fall within the spectral ranges covered by several new astronomical observatories, including the *HIFI* instrument on the Herschel Space Observatory, the *GREAT* instrument on the Stratospheric Observatory for Infrared Astronomy (SOFIA), and the Atacama Large Millimeter Array (ALMA). The high resolution and high sensitivity of these instruments should greatly enhance the prospect of definitive astronomical detections of these species. This is a key step in furthering our understanding of the formation of complex organic species, of which H_5^+ is thought to be a key precursor. Furthermore, the mechanisms for deuterium fractionation in interstellar environments are greatly influenced by the ortho/para ratio of H_3^+ and H_2 . These ortho/para ratios have been shown through recent work¹⁴ to be driven largely by the reaction $\text{H}_3^+ + \text{H}_2 \rightarrow \text{H}_5^+ \rightarrow \text{H}_2 + \text{H}_3^+$.

We have presented here the ZP-averaged structures, rotational constants, dipole moments, and predicted spectra for H_5^+ and its isotopologues based on the most rigorous theoretical treatment of this ion to date. These results show promise for the possibility of detecting H_2D_3^+ , H_3D_2^+ , and H_4D^+ both in the laboratory and in space. These spectral predictions serve as an initial guide

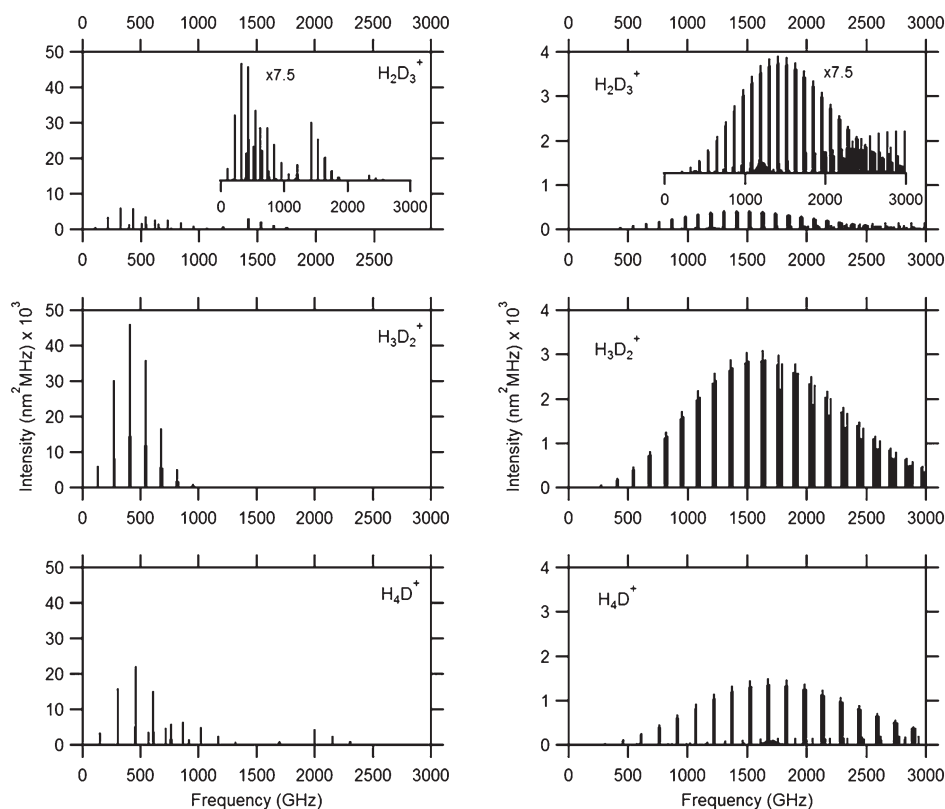


Figure 2. Simulated rotational spectra of H_2D_3^+ , H_3D_2^+ , and H_4D^+ at 20 K (left) and 300 K (right). The insets for H_2D_3^+ spectra show the spectral detail.

for pure rotational laboratory studies of these ions. Additional theoretical studies that further investigate the contributions of the fluxional behavior of these ions to their spectral complexity will also be required before their spectra can be fully interpreted.

■ ASSOCIATED CONTENT

S Supporting Information. Full spectral catalogs in the standard CALPGM format for each species at 300 K and tables reporting the bond lengths of each species. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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