Communication: Rigidity of the molecular ion H_5^+

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The fourth-age quantum chemical code GENIUSH is used for the variational determination of rotational-vibrational energy levels corresponding to reduced- and full-dimensional models of H_5^+, a molecular ion exhibiting several strongly coupled large-amplitude motions. The computations are supplemented with one- and two-dimensional analytic results which help to understand the peculiar rovibrational energy-level structure computed correctly for the first time. An unusual aspect of the results is that the canonical Eckart-embedding of molecule-fixed axes, a cornerstone of the computational spectroscopy of semirigid molecules, is found to be inadequate. Furthermore, it is shown that while the 1D "active torsion" model provides proper results when compared to the full, 9D treatment, models excluding the torsion have limited physical significance. The structure of the rovibrational energy levels of H_5^+ proves that this is a prototypical astructural molecule: the rotational and vibrational level spacings are of the same order of magnitude and the level structure drastically deviates from that computed via perturbed rigid-rotor and harmonic-oscillator models. [http://dx.doi.org/10.1063/1.4864360]

The term "quasimolecule," as found in the book of Kroto on molecular rotation spectra,[1] refers to nonrigid species for which the magnitude of displacement vectors from an assumed equilibrium structure considerably exceeds, in a somewhat loose sense, the vectors characterizing the equilibrium structure even for the lowest nuclear motion states. These days this term finds usage to describe extremely unusual molecular systems where the notion of a molecule is questioned (e.g., molecular systems stripped of (most of) their electrons). Back to the rigidity of "real" molecules, the terms "polytopic bonds" and "polytopic molecules" describe systems with weak internal bonding where multiple, energetically close-lying isomers are separated by low barriers resulting in overly large amplitude internal motions.[2] Lower-symmetry polytopic systems include LiCN[2] and KCN,[3] while a more symmetric example is SiC_2.[4]

Supplementing the terms "quasimolecule" and "polytopic molecule," we introduce here the term "astructural molecule," referring to a class of species where the utility of an equilibrium structure is questioned. Some of the collision complexes, quasilinear and quasiplanar molecules,[5] and nonclassical carbonium ions[6] could be thought of as astructural molecules. Classifying a molecule as astructural is not simple. Take, for example, toluene, a one-top molecule with an extremely low barrier to internal rotation. Toluene may not be a true astructural molecule in the eyes of most chemists but it is one example where interpretation of the pure rotational spectrum is problematic with standard theory,[1] and the effective rotational constants of the molecule are not simply related to the equilibrium rotational constants.[7] It is suggested that for an astructural molecule rotational and vibrational spacings are of the same magnitude, the usual simple traditional tools of quantum chemistry,[1] rigid rotors (RR) and harmonic oscillators (HO), are unable to yield a reasonable estimate of even the lowest rotational and rovibrational energy levels, and simple perturbative treatments based on the RRHO approximation fail already for the lowest nuclear motion states. As a consequence, the structure averaged over the vibrational ground state of astructural molecules is significantly different from the equilibrium Born–Oppenheimer one. As shown here, it is hard to find a more suitable candidate for the class of astructural molecules than H_5^+.

The nuclear dynamics of the astructural molecular ion H_5^+ exhibits a number of unusual features. Due to the lightness of the H atom, many of the vibrations of H_5^+ are of very large amplitude, separation of the vibrational and rotational degrees of freedom (dof) is poor, calling particular attention to the embedding of the molecule-fixed rotation axes, adiabatic and nonadiabatic effects are expected to become overly important, similar to H_3^+,[8–10] and the usual perturbational treatments and effective Hamiltonians have extremely poor convergence characteristics. Therefore, only variational nuclear motion techniques are suitable for the interpretation of the complex rotational-vibrational spectra of these ions. Sophisticated techniques have indeed been developed to treat bound and quasibound rovibrational states of molecules of arbitrary flexibility during the fourth age of quantum chemistry.[11]

A number of quantum chemical techniques have been used to characterize the structure and dynamics of H_5^+.[12–19] These studies resulted in a number of peculiar observations.

The twisted equilibrium structure of the ground electronic state of H_5^+ can be described[12–14] as a complex of H_3^+ and H_2, corresponding to C_{2v} point-group symmetry (Figure 1). Acioli *et al.*[15] predicted a zero-point-averaged effective structure of D_{2d} point-group symmetry, suggesting that in the ground state the H_5^+ cation does not differentiate,

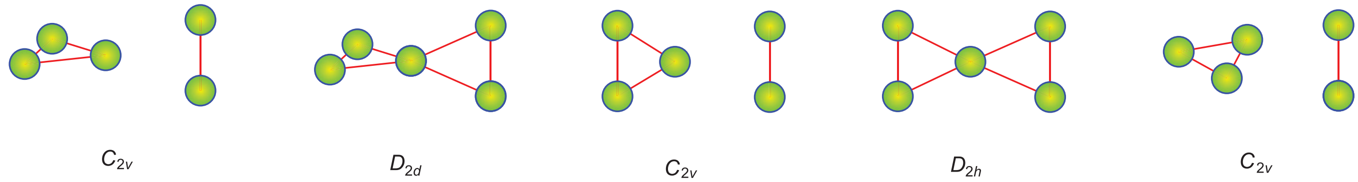

FIG. 1. Five stationary points on the PES of H_5^+ of highest relevance for the present study. Only the first C_{2v} structure corresponds to a minimum.

unlike in its equilibrium structure, between the two H_2 units.

H_5^+ effectively rotates as a prolate symmetric top. For any of the lowest four stationary points on the potential energy surface (PES) of H_5^+ (Figure 1) computed *ab initio*, the rotational constants B and C are about 3.3, while A is about 26.7 cm^{-1}. McGuire *et al.*[16] investigated whether H_5^+, and its deuterated isotopologues, would have pure rotation spectra. They predicted, based on diffusion Monte Carlo (DMC) computations, that the zero-point averaged dipole moment of H_5^+ is zero; thus, the ion does not exhibit a rotational spectrum. The lack of a dipole moment is due to the effectively D_{2d}-like structure of the ion. Recently, Lin and McCoy[18] computed vibrationally averaged rotational constants and dipole moments via a reduced-dimensional model of questionable quality (*vide infra*) based on freezing the torsional motion. To summarize the literature results, the equilibrium and the zero-point averaged structures and the low-energy vibrational dynamics of H_5^+ seem to be relatively well characterized by first-principles computations. Nevertheless, the rovibrational energy levels have not been determined by dependable variational nuclear motion computations.

There are two accurate (semi)global PESs available for H_5^+.[13,14] The internal dynamics of H_5^+ can be characterized by three large-amplitude motions with low barriers.[12–14] The first and foremost is the torsional motion of the two formal H_2 units with respect to each other. The electronic barrier to this motion is 95 cm^{-1}.[14] H_5^+ is characterized by a symmetric and antisymmetric torsional mode, ν_{TE} and ν_{TO}, respectively. The second is the hopping motion of the central proton, the associated fundamental is denoted as ν_{PH}, switching the left- and right-hand sides of the molecule. The electronic barrier to this motion is a mere 64 cm^{-1}.[14] The third motion is the internal rotation of the formal H_3^+ unit, which can be described as a scrambling mode, ν_{SC}. The electronic barrier to this motion is about 1500 cm^{-1}.[14] These motions are responsible for a possible interchange of the "numbered" positions of the atoms of the ion. A fourth large-amplitude motion also exists: separation of the two formal H_2 diatoms.

In order to understand the internal dynamics of H_5^+, it is important to be able to treat reduced-dimensional models with relative ease. This facility is readily provided by the fourth-age quantum chemical protocol GENIUSH,[20–22] employed extensively in this work. Details about GENIUSH and the nuclear motion computations performed are provided in the original publications and the supplementary material;[23] we mention here only the most important points. First, it is essential to choose the best internal coordinates to describe the vibrational motions. The set shown in Figure 2 turned out to be far superior to all other coordinate systems tried. Second, the Eckart-embedding,[24] one of the cornerstones of the traditional theory of nuclear motions, is not adequate to treat the rovibrational coupling present in H_5^+, as proven both by reduced- and full-dimensional computations. For example, with an Eckart-embedding the one-dimensional (1D) torsion model, with all other dof frozen at their equilibrium values, does not show the same rotational structure as the full-dimensional treatment, the rotational energies are compatible with a rigid-rotor model. A flexible Eckart-embedding,[25] whereby the reference structure follows the torsional motion, becomes an adequate model for the joint treatment of rotations and vibrations. Another adequate embedding of the rotating axes, used throughout this study, is shown in Figure 2. Third, choice of the basis functions, in particular choice of the grid intervals, is crucial for our ability to obtain converged results with relatively few basis functions along each coordinate. The choices detailed in the supplementary material[23] proved to be close to ideal for the lower states computed, and are based on a large number of reduced-dimensional computations and the careful investigation of the corresponding wave function plots.

From preliminary variational treatments it became obvious that a simple 1D model, when only the torsional motion is active, is of special interest and works surprisingly well when compared to the full (9D) treatment (Tables I and II). In order to understand the rovibrational energy level structure of H_5^+, we carried out a detailed analysis of the 1D torsion-only model. As detailed in the supplementary material,[23] coupling the ϕ "active" torsion to the three rotation degrees of freedom leads to the effective rotational constants $A = \frac{1}{mr^2}$ and $B = \frac{1}{m(r^2+2R^2)}$, where r and R stand for the fixed distance of the two hydrogens in the H_2 diatoms and the distance of the midpoints of the two diatoms, respectively. When comparing these values to $A_{\rm ref} = \frac{1}{2mr^2}$ and $B_{\rm ref} = \frac{1}{m(r^2+2R^2)}$

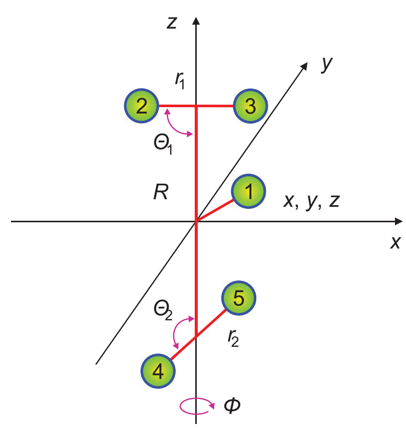

FIG. 2. Internal coordinates and body-fixed frame embedding of H_5^+ employed during this study.

TABLE I. The lowest eight vibrational band origins of H_5^+.[a]

Assignment	1D(ϕ)	2D(ϕ, z)	2D(R, z)	3D(R, ϕ, z)	9D	Ref. 17	Ref. 18	Ref. 19
$\nu_{ZP} \equiv$ ZPVE	236.6	494.0	1097.5	1144.5	7237.6	7237.5	7234.1	7214.6
ν_{TE}	87.9	86.3		84.6	89.9	90.9		87.3
ν_{TO}	128.3	130.5		132.7	135.8	136.2		138.7
ν_{PH}		870.6	693.7	686.1	352.3	353.5	356	354.4
$2\nu_{TE} \equiv \nu_{2TE}$	429.1	429.4		429.8	446.3	449.4		444.0
$2\nu_{TO} \equiv \nu_{2TO}$	429.4	430.1		430.7	446.9	452.1		446.8
$\nu_{TE} + \nu_{PH}$		955.2		774.0	445.6	449.7		447.3
$\nu_{TO} + \nu_{PH}$		1003.6		814.4	483.0	486.7		486.3

[a]ZP = zero-point vibration, TE = torsion (even), TO = torsion (odd), PH = proton hopping. The reduced dimensional models are described in detail in the text, the corresponding VBOs are fully converged. Valdes *et al.*[17] and Lin *et al.*,[18] as well as this work, applied the PES developed by Aguado *et al.*[14] Song *et al.*[19] applied the PES developed by Xie *et al.*[13] ϕ denotes the "torsion" coordinate, R the separation of the two formal diatom units, and z describes the proton hopping motion. See Figure 2 and the text for further details.

computed from the reference structure it becomes evident that A is twice as large as its traditional $A_{\rm ref}$ counterpart. This doubling is due to the substantial coupling of the low-frequency torsional mode with a rotational dof. This is a key result of this study and has a profound effect on the spacing of the rovibrational states of H_5^+. It almost in itself explains the astructural character of H_5^+.

Taking the rovibrational coupling into account, a corrected rigid rotor (CRR) formula,

$$E_{JK}^{\rm RR} + \frac{E_{v^+} + E_{v^-}}{2} \pm \sqrt{\frac{(E_{v^+} - E_{v^-})^2}{4} + A_{v^+v^-}^2 K^2}, \qquad (1)$$

can be derived, as detailed in the supplementary material.[23] It applies to the 1D torsion model but provides a good approximation for the variational rovibrational energy levels computed in this work (Table II). In the CRR formula, $A_{v^+v^-}$ is a rovibrational coupling matrix element between the $|v^+\rangle$ and $|v^-\rangle$ vibrational states of the distinct torsional doublets, $\hat{H}_{\rm v}|v\rangle = E_v|v\rangle$, where $\hat{H}_{\rm v}$ is the vibrational Hamiltonian, $E_{JK}^{\rm RR} = BJ(J+1) + (A-B)K^2$, and (JK) are rotation quantum numbers.[1] Moreover, variational rovibrational energy levels with $K = 0$ correspond to rotational energies obtained with the $E_{J0}^{\rm RR} = BJ(J+1)$ symmetric top formula, which is also supported by Eq. (1).

Proton hopping (z coordinate, Figure 2) can also be studied in 1D. This model, however, results in large deviations when compared to the 9D energies. This indicates that the effective hopping motion is not separated well from the other

TABLE II. $J = 1$ and 2 rotational energies, and their characterization, of H_5^+ in reduced and full dimensions.[a]

VBO	J	$\|K\|$	RR_1	RR_2	CRR	1D(ϕ)	Mixing	2D(R, z)	9D
ν_{ZP}	1	0	6.7	6.7	6.7	6.7	$1.00\nu_{ZP}$	6.6	6.4
		1	30.0	56.7	56.7	56.0	$0.50\nu_{ZP}+0.30\nu_{TE}+0.20\nu_{TO}$	30.0	57.8
	2	0	20.0	20.0	20.0	20.0	$1.00\nu_{ZP}$	19.9	19.3
		1	43.3	70.0	70.0	69.2	$0.50\nu_{ZP}+0.30\nu_{TE}+0.20\nu_{TO}$	43.3	70.4
		2	113.3	220.0	220.0	201.3	$0.55\nu_{ZP}+0.24\nu_{2TE}+0.22\nu_{2TO}$	113.3	205.2
ν_{TE}	1	0	6.7	6.7	6.7	6.7	$1.00\nu_{TE}$		6.4
		1	30.0	56.7	− 31.8	− 31.8	$0.50\nu_{ZP}+0.30\nu_{TE}+0.20\nu_{TO}$		− 32.1
	2	0	20.0	20.0	20.0	20.1	$1.00\nu_{TE}$		19.2
		1	43.3	70.0	− 18.5	− 18.2	$0.50\nu_{ZP}+0.30\nu_{TE}+0.20\nu_{TO}$		− 19.2
		2	113.3	220.0	25.6	25.4	$0.55\nu_{TE}+0.45\nu_{TO}$		27.8
ν_{TO}	1	0	6.7	6.7	6.7	6.6	$1.00\nu_{TO}$		6.4
		1	30.0	56.7	145.2	145.1	$0.20\nu_{TE}+0.30\nu_{TO}+0.25\nu_{2TE}+0.25\nu_{2TO}$		148.1
	2	0	20.0	20.0	20.0	20.0	$1.00\nu_{TO}$		19.2
		1	43.3	70.0	158.5	158.4	$0.20\nu_{TE}+0.30\nu_{TO}+0.25\nu_{2TE}+0.25\nu_{2TO}$		160.2
		2	113.3	220.0	414.4	414.2	$0.24\nu_{TE}+0.26\nu_{TO}+0.25\nu_{3TE}+0.25\nu_{3TE}$		416.8
ν_{PH}	1	0	6.7	6.7				6.1	5.7
		1	30.0	56.7				29.7	58.2
	2	0	20.0	20.0				18.2	17.0
		1	43.3	70.0				41.9	69.2
		2	113.3	220.0				112.8	

[a]The rigid-rotor RR_1 and RR_2 and the corrected rigid rotor (CRR) models are explained in the text. The RR estimates were obtained with the following rotational constants: $A = 26.67$ and $B = C = 3.33$ cm^{-1} for RR_1 and $A = 53.34$ and $B = C = 3.33$ cm^{-1} for RR_2. All rovibrational states reported are referenced to the respective VBOs, whose values are reported in Table I. This explains the occasional occurrence of "negative" rotational energies. "Mixing" refers to results of the RRD analysis of the 1D(ϕ) model. In the mixing expressions, the J and K labels of the energy level are given in the second and third columns within the given row. For further notational details see also the footnote to Table I.

internal motions. The Eckart-barrier model[26] provides a simple way to treat tunneling dynamics along one dimension. This model, however, cannot be used to study the proton hopping dynamics of H_5^+ as the barrier disappears when zero-point energy corrections are applied to the stationary points characterizing this motion. This is yet another peculiar feature of the PES of H_5^+.

Beyond the 1D models mentioned it is relevant to discuss a 2D (R, z) model (Figure 2), where r is kept fixed, and ϕ is set to its equilibrium value to eliminate the strong torsion-rotation coupling. As detailed in the supplementary material,[23] this 2D model yields effective rotational constants coinciding with A_{ref} and B_{ref}. We can conclude that (a) this 2D model does not possess the interesting peculiarities of the 1D torsional model as the motion along ϕ is constrained; and (b) the rigid rotor approximation provides a good description for the rovibrational energy levels computed with the 2D (R, z) model. These 2D results, as well as other reduced-dimensional model results not detailed here, suggest that only those reduced-dimensional models should be accepted as physically relevant where the torsional motion is active, all other simplified treatments make limited physical sense and their results should be viewed with extreme caution. Thus, the rotational spectra of certain isotopologues of H_5^+ predicted by McGuire *et al.*[16] as well as the effective rotational constants determined by Lin and McCoy[18] should be viewed with care as they are based on overly simplified models to treat the internal dynamics.

The principal goal of this study is the determination of accurate rotational-vibrational energy levels of H_5^+. The vibration-only levels (Table I) are in good agreement with previous 9D investigations.[17–19] As to rotations, this is the first time that results from full-dimensional variational rovibrational computations are reported for this ion.

It is important not only to determine but also to understand the 12D variational results, i.e., the energy levels and the associated wavefunctions. The simplest approach to assign the rovibrational energy levels is based on the RR model (Table II). This works well for all semirigid molecules[1] and even for a large number of molecules exhibiting large-amplitude motion. Within the RR model the rotational constants of the equilibrium structure, of C_{2v} point-group symmetry, as well as the rotational constants of the symmetric stationary points of D_{2d} or D_{2h} symmetry (Figure 1) can be used. The associated energy levels are called RR_1 in Table II. As Table II shows there are remarkable deviations between the full-dimensional variational and the RR_1 results for the $K \neq 0$ energy levels. These large deviations are due to the coupling between the rotational dofs and ϕ. Taking this coupling into account allows the use of a more sophisticated RR model, called RR_2, whereby the A rotational constant is doubled as compared to RR_1 (see the supplementary material[23]). It is clear that once the strong interaction of the torsional mode and a rotational dof is taken into account the rotation energies can be explained in a much more satisfactory way even by a RR model. For the zero-point vibration (ν_{ZP}), the RR_2 model provides rotation energies in good agreement with their variational counterparts. Nevertheless, for excited vibrational states both the RR_1 and RR_2 models fail, in accordance with the astructural nature of H_5^+.

The approximate CRR formula (Eq. (1)) modeling the 1D torsion motion gives results in considerably better agreement with the variationally computed results (column CRR in Table II). The data clearly show the utility of a corrected rigid-rotor model where the torsion-rotation interaction is taken into account via a simple one-dimensional model for a system where the rotational and vibrational spacings are of the same magnitude.

Looking at the $J \neq 0$ energy levels, referenced to the respective vibrational band origins (VBO), of the 1D torsional and 9D models of H_5^+ in more detail, negative rotational increments can be observed (Table II). For example, the $J = 1$ and $K \neq 0$ energy levels for the first and second VBO, ν_{ZP} and ν_{TE}, respectively, become nearly degenerate, as can be seen more clearly for the H_5^+ data presented in Table 3 of the supplementary material.[23] Similar near degeneracies exist for higher J values and for the 1D and 9D $K \neq 0$ energies for ν_{TO} and $2\nu_{\mathrm{TE}}$, as well. Furthermore, the $2\nu_{\mathrm{TE}}$ and $2\nu_{\mathrm{TO}}$ vibrational levels, as well as the $K \neq 0$ rovibrational energies on them become near degenerate (marked as $2\nu_{\mathrm{TE/TO}}$ in Table 3 of the supplementary material). These near degeneracies constitute even another highly unusual feature of the rovibrational energy level structure of H_5^+.

Supplementing results obtained with the CRR model with a rigid-rotor decomposition (RRD)[27] analysis helps to secure the assignment of the variationally computed rovibrational states. Utilizing the RRD analysis in the 1D torsion model, heavy mixing of the different VBOs with the same J and $|K|$ quantum numbers is found for all the $K \neq 0$ rovibrational energy levels. These interesting mixings, detailed in Table II, point once again toward the peculiar nature of the internal dynamics of H_5^+.

In conclusion, the rovibrational energy levels of H_5^+ display several highly peculiar characteristics. The rovibrational energy level structure seems to be sufficient to characterize H_5^+ as an astructural molecule: the rotational and vibrational spacings are of the same magnitude and there is substantial deviation between the variational rovibrational energy levels and their RR counterparts, except for $K = 0$. The reduced-dimensional computations also point out the very limited applicability of certain simplified models, especially those where the torsional motion is not considered. 1D analytical models are able to explain the two main reasons for the large deviations: the A rotational constant of the molecule is twice as large as the A_{ref} value computed from the effective "equilibrium" structure and there is an extremely strong coupling between the torsional and rotational degrees of freedom. The use of the rigid rotor decomposition scheme allows the analysis of the rovibrational wave functions computed and provides insight into the extreme mixing of the rovibrational states.

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[23] See the supplementary material at http://dx.doi.org/10.1063/1.4864360 for additional documentation regarding (I) extensions to Table II; (II) $J = 1$ rovibrational energies of H_5^+ (Table 3); (III) computational details, including Table 4; (IV) derivation of rotational constants within the RR_2 model; (V) derivation of the corrected rigid rotor (CRR) formula, Eq. (1); (VI) derivation of the 2D (R, z) model.
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