



Application of nuclear permutation inversion group theory to the benzenium ion

Brian E. Brumfield^a, Benjamin J. McCall^{b,*}

^a Department of Chemistry, University of Illinois, 600 South Mathews Avenue, Urbana, IL 61801, USA

^b Departments of Chemistry and Astronomy, University of Illinois, Urbana, IL 61801, USA

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This article is dedicated to Phil Bunker in appreciation of the significant contributions he has made to developing, applying, and communicating the use of the molecular symmetry group to problems in molecular spectroscopy.

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ABSTRACT

Nuclear permutation-inversion (PI) group theory and the linear combination of localized wavefunctions (LCLW) method are applied to the proton “ring-walk” tunneling problem in $C_6D_6H^+$ and the benzenium ion ($C_6H_7^+$). For $C_6D_6H^+$ and $C_6H_7^+$, the rigid and non-rigid MS groups are developed, and their corresponding correlation tables constructed. The reverse correlation relationship is combined with spin statistical restrictions to determine the number of allowed tunneling split levels for both ions. Through the use of the LCLW method and the WKB approximation, the qualitative pattern of the tunneling splitting is presented for $C_6D_6H^+$. Application of the LCLW problem for the benzenium ion is presented, but the complete treatment to obtain the structure of the tunneling split levels is limited by the computational expense of obtaining the eigenvectors from the diagonalization of the $15\,120 \times 15\,120$ connectivity matrix.

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1. Introduction

The benzenium ion ($C_6H_7^+$) is the prototypical arenium ion intermediate in electrophilic aromatic substitution (EAS) reactions [1]. As a key intermediate, the benzenium ion has been the focus of a variety of experimental and theoretical studies probing the structure, reactivity, and intramolecular dynamics. These studies include 1H and ^{13}C NMR work in cold superacid media [2,3], infrared photodissociation spectroscopy [4–6], infrared multiphoton dissociation spectroscopy (IRMPD) [7], radiolytic methods [8], mass spectroscopy [9,10], and theoretical work [11–14].

The benzenium ion is also of interest to the astrochemical community. It is considered a key intermediate in the proposed reaction pathways for the synthesis of benzene in dense interstellar clouds and proto-planetary nebulae [15,16]. Benzene has already been detected in proto-planetary nebula CRL618 [17], increasing the likelihood that the benzenium ion is present in the same environment. The larger class of protonated polycyclic aromatic hydrocarbons, of which the benzenium ion is the prototype, has also been proposed as carriers of the unidentified infrared bands [18–20].

Both theory and experiment agree that the equilibrium structure for the ion is of C_{2v} point group symmetry, as shown in Fig. 1. The intramolecular dynamics of the ion are dominated by

a 1,2-H shift, termed the proton “ring-walk” (Fig. 2). The activation energy barrier for the 1,2-H shift is estimated from condensed phase superacid NMR measurements to be 10 ± 1 kcal/mol ($G^\ddagger \sim 8$ kcal/mol) [2,3]. Estimates of the energy barrier from theory are around 8 kcal/mol (~ 2800 cm^{-1}) [11–14].

In the literature there are no reports of high-resolution infrared or microwave spectra of the benzenium ion. This is likely due to the technical challenge of generating a sufficient number density of the ion to permit direct spectroscopic detection. A high-resolution infrared or microwave spectrum of the benzenium ion may show an extensive number of tunneling splittings because of the “ring-walk” pathway. A crude estimate for the magnitude of the tunneling splitting can be made with a simplistic double-well WKB approximation:

$$\tilde{\nu}_{splitting} \text{ (cm}^{-1}\text{)} = \frac{\tilde{\nu}_0}{\pi} e^{-\frac{1}{\hbar} \int_{-a}^a \sqrt{2m_p(U(x)-E)} dx} \quad (1)$$

where $\tilde{\nu}_{splitting}$ is the estimated energy splitting from a proton tunneling through the potential energy barrier, m_p is the mass of the proton, a is half the distance across the barrier, and $\tilde{\nu}_0$ is the attempt frequency. For $(U(x) - E)$, the [one-dimensional] potential energy barrier minus the kinetic energy of the particle, we adopt a form $hc\tilde{\nu}_{barrier}(1 - x^2/a^2)$, and then integrate to arrive at:

$$\tilde{\nu}_{splitting} \text{ (cm}^{-1}\text{)} = \frac{\tilde{\nu}_0}{\pi} e^{-\frac{a\pi}{2\hbar} \sqrt{2m_p hc \tilde{\nu}_{barrier}}} \quad (2)$$

To estimate the order of magnitude of the splitting that results from a proton tunneling to an adjacent carbon on the benzene ring, we

* Corresponding author.

E-mail addresses: bbrumfi2@illinois.edu (B.E. Brumfield), bjmccl@illinois.edu (B.J. McCall).

assume rough values of $a \sim 7 \times 10^{-9}$ cm (half of benzene's C–C bond length), $\tilde{\nu}_0 \sim 1000$ cm^{-1} (a typical vibrational frequency for the bending or wagging modes of a C–H moiety), and $\tilde{\nu}_{\text{barrier}} \sim 2800$ cm^{-1} (an average value from the various experimental

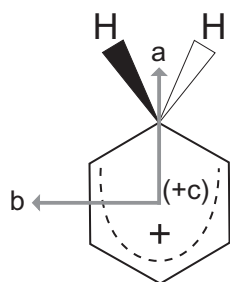


Fig. 1. Diagram showing the rigid $C_{2v}(M)$ structure of the benzenium ion. The principal a , b , and c axes are labeled. Only the methylene hydrogens are shown in this figure.

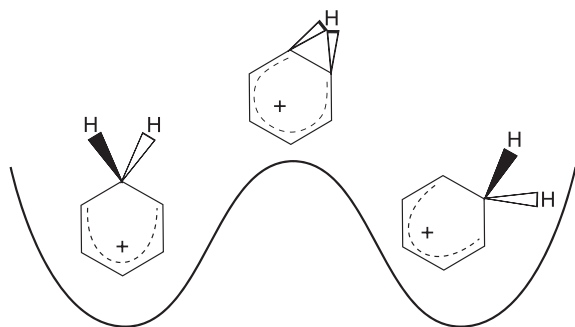


Fig. 2. Example of proton tunneling in the benzenium ion.

and theoretical studies). Given these values, we find an estimated splitting of 2×10^{-4} cm^{-1} (6 MHz), which is large enough to be observed in an infrared or microwave experiment.

If the tunneling splitting in the ion is resolved experimentally, it would be useful to apply nuclear permutation inversion (PI) group theory to aid in the assignment of the spectra by providing details such as the number of expected tunneling splittings and statistical weights. The analysis of the high-resolution tunneling spectra could then provide information that would allow a more accurate determination of the proton “ring-walk” potential barrier. Understanding of the tunneling dynamics of the benzenium ion could also aid in future studies probing mono-substituted benzenium ions examining the influence of ortho/para and meta directors on the proton “ring-walk” tunneling problem.

There has been no attempt in the literature to apply PI theory to garner a better understanding of the non-rigid benzenium ion. Here, we seek to present a starting point for application of MS group theory for the benzenium ion. In the second section, we explore the feasibility of the proton tunneling pathway with the isotopologue $C_6D_6H^+$. This isotopologue generates a much smaller non-rigid MS group than the non-rigid benzenium ion because the tunneling of the deuterons can be neglected on the basis of their increased mass. The reverse correlation is applied to $C_6D_6H^+$ to determine the number of times that a rotational level in the rigid ion will split when tunneling is considered. The linear combination of localized wavefunctions (LCLW) [21] approach is applied to obtain a qualitative estimate of the splitting pattern due to proton tunneling. In the third section, the treatment developed for the $C_6D_6H^+$ ion will be applied to the rigid and non-rigid benzenium ion. The number of times that a ground state rotational level of the non-rigid benzenium ion is expected to split due to the proton “ring-walk” tunneling motion is determined. The LCLW method is developed for the complex case of the non-rigid benzenium ion.

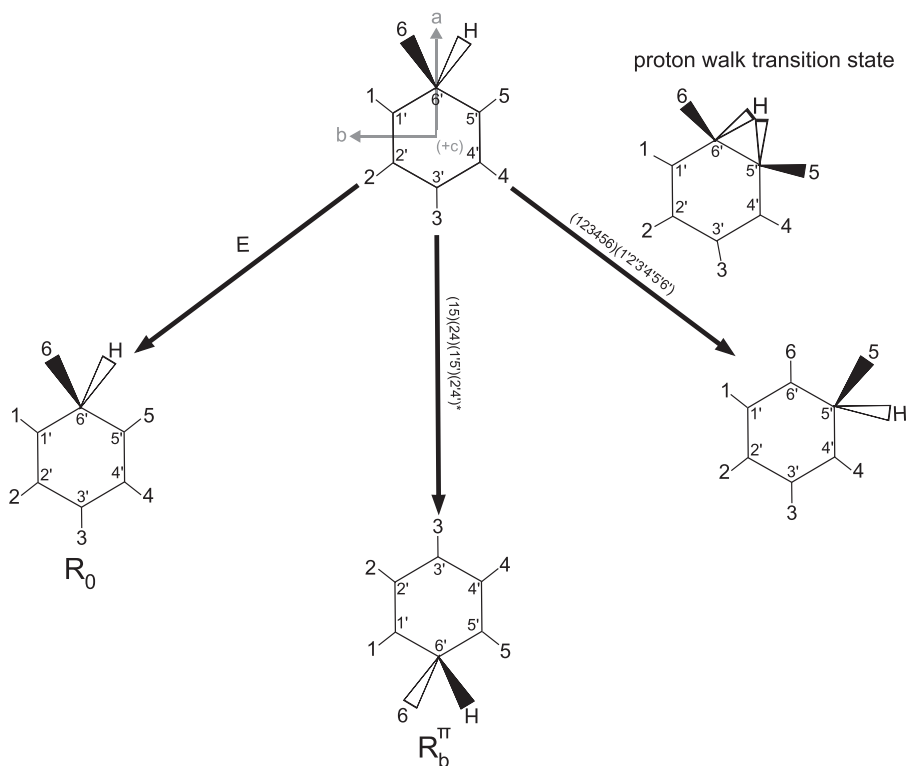


Fig. 3. The feasible operations and principal axes are presented for $C_6D_6H^+$. The small displacement and tilt of the center of mass and the principal a -axis with respect to the benzenium ion is neglected. For treatment of the rigid ion both the E and $(15)(24)(1'5')(2'4)^*$ are part of the molecular symmetry group C_s . The feasible tunneling operation $(123456)(1'2'3'4'5'6')$ is shown to the far right.

The connectivity matrix for the problem is diagonalized, but only the eigenvalues for the problem are obtained due to the significant increase in the computational expense of obtaining all the eigenvectors.

2. Rigid and non-rigid $C_6D_6H^+$

The singly protonated d_6 -benzene ion ($C_6D_6H^+$) will be analyzed first, illustrating the application of the reverse correlation, nuclear spin statistics, and the LCLW method to the problem of a single proton walking around the six membered ring.

To determine the rigid molecular symmetry group for the C_s equilibrium structure of $C_6D_6H^+$, we need to find the feasible PI operations. The feasibility [22] of an operation depends on the resolution of the experiment and on the height of the energy barrier separating structurally degenerate (but differently labeled) versions of the equilibrium structure that are connected by that particular operation. If the experimental resolution is insufficient to resolve the tunneling splittings associated with some operation, then that operation is considered unfeasible. Our treatment of the rigid $C_6D_6H^+$ ion corresponds to what one would observe in an experiment at relatively low resolution, where the “ring-walk” tunneling splittings are not resolved. In this limit, we must exclude PI operations that convert one structure, with the nuclei labeled in one particular way, into differently labeled versions that cannot be transformed back to the original by a simple rotation of the equilibrium geometry.

The labeling used for the equilibrium structure of rigid $C_6D_6H^+$ is presented at the top of Fig. 3. The two feasible operations, in the absence of a proton tunneling pathway, are E and $(15)(24)(1'5')(2'4')$. These operations are both shown in Fig. 3. The corresponding character table for the molecular symmetry group is provided in Table 1.

The non-rigid molecular symmetry group for the $C_6D_6H^+$ can be considered by allowing for the feasibility of the proton “ring-walk” pathway. The proton/deuteron “ring-walk” pathway for $C_6D_6H^+$ ion is the same as that shown in Fig. 2, except the transition state and equilibrium structure are both of C_s point group symmetry. A bridged intermediate provides the transition state in the pathway for proton/deuteron transfers between adjacent carbon atoms in the ring. For each equilibrium geometry, either the top or bottom

deuteron/proton could tunnel one carbon clockwise or counter-clockwise around the ring. Subsequent tunneling through other equivalent transition states allows the proton/deuteron to “walk” around the ring, and can lead to the scrambling of the protons and the deuterons around the ring. As discussed earlier, the estimated barrier for this tunneling process is ~ 8 kcal/mol (~ 2800 cm^{-1}).

For $C_6D_6H^+$, only the proton is permitted to “walk” around the six membered carbon ring due to the increased mass of the deuterons. Inserting the mass of the deuteron into Eq. (2), the calculated tunneling splitting from the WKB approximation is $\sim 6 \times 10^{-7}$ cm^{-1} (18 kHz). Such splittings would be difficult to resolve experimentally, so we consider the 1,2-D shift to be unfeasible. This reduces the problem to that of a single proton executing a “ring-walk” motion around the 6-membered carbon ring.

The proton “ring-walk” motion for the non-rigid ion can be thought of as a $(123456)(1'2'3'4'5'6')$ operation, “leaving” the single proton behind. The result of this PI operation is shown on the right side of Fig. 3. The non-rigid MS group for $C_6D_6H^+$ can be created by using $(15)(24)(1'5')(2'4')$ and $(123456)(1'2'3'4'5'6')$ as the group generators. The resulting MS group for non-rigid $C_6D_6H^+$ ion is G_{12} , and is isomorphic with the point group C_{6v} ; its character table is shown in Table 2. The corresponding point group operations for C_{6v} are below the MS group operations. The equivalent rotations listed in Table 3 for G_{12} are determined by treating $C_6D_6H^+$ as an internal rotor problem, where the proton and the center of mass represent the rigid frame, and the C_6D_6 portion of the molecule is treated as the free rotor. The equivalent rotations for the G_{12} group will be used when the LCLW method is applied to $C_6D_6H^+$.

The equivalent rotations found in Tables 1 and 2 are useful for identifying the symmetry labels for the irreducible representations for the asymmetric top wavefunctions ($\Gamma_{J_{K_a K_c}}$). This can be done by applying the asymmetric top rule [23], which relates the characters of the equivalent rotations to the symmetry labels of asymmetric top wavefunctions based on the parity (even- or odd-ness) of the K_a and K_c quantum numbers. The result of the application of this rule to the rigid and non-rigid $C_6D_6H^+$ ion are shown in Table 3. Knowledge of the symmetry labels of $\Gamma_{J_{K_a K_c}}$ in the rigid group will be necessary for assigning the number of times a particular rigid ground state rotational level will split due to the proton “ring-walk” tunneling in the non-rigid ion.

Table 1
 $C_s(M)$ character table for the rigid $C_6D_6H^+$, including the corresponding equivalent rotations and point group operations.

$C_{2d}(M)$	E	$(15)(24)(1'5')(2'4')$ *
C_s	E	σ_v
Order	1	1
Equiv. rot.	R_0	R_b^π
A'	1	1
A''	1	-1

Table 2
 G_{12} character table for the non-rigid $C_6D_6H^+$ ion, including the corresponding C_{6v} point group operations.

G_{12}	E	(123456) $(1'2'3'4'5'6')$	$(135)(246)$ $(1'3'5')(2'4'6')$	$(14)(25)(36)$ $(1'4')(2'5')(3'6')$	$(26)(35)$ $(2'6')(3'5')$ *	$(12)(36)(45)$ $(1'2')(3'4')(4'5')$ *
C_{6v}	E	C_6	C_3	C_2	σ_v	σ_d
Order	1	2	2	1	3	3
Equiv. rot.	R_0	R_0	R_0	R_0	R_b^π	R_a^π
A_1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1
B_1	1	-1	1	-1	1	-1
B_2	1	-1	1	-1	-1	1
E_1	2	1	-1	-2	0	0
E_2	2	-1	-1	2	0	0

Table 3
Application of the asymmetric top rule for rigid and non-rigid $C_6D_6H^+$.

$J_{K_a K_c}$	$C_s(M)$	G_{12}
J_{ee}	A'	A_1
J_{eo}	A''	B_2
J_{oe}	A''	A_2
J_{oo}	A'	B_1

We now aim to determine how many times an asymmetric top level in the ground electronic and vibrational state for the rigid ion will split due to the “ring-walk” tunneling motion. To do this we will construct a correlation table, taking advantage of the fact that the $C_s(M)$ MS group for the rigid ion is a subgroup of G_{12} . This provides a link between the rigid and non-rigid molecular symmetry groups for the ion. The correlation between an irreducible representation in G_{12} to $C_s(M)$ can be determined by using the following relationship [23]:

$$a_i^\alpha = \frac{1}{h} \sum_{r=1}^h \chi^{r\alpha}[H_r] \chi^{r_i}[H_r]^* \quad (3)$$

where a_i^α is the coefficient that indicates how many from the i th irreducible representation of $C_s(M)$ are in the reduction of the α irreducible representation in G_{12} , h is the order of the subgroup $C_s(M)$, $\chi^{r\alpha}[H_r]$ is the character for the representation in the G_{12} symmetry group for the shared element r , and $\chi^{r_i}[H_r]^*$ is the complex conjugate of the character for the irreducible representation in the group $C_s(M)$. The summation is carried out over the characters for the PI operations in $C_s(M)$ that are also found in G_{12} .

Application of Eq. (3) over the 2 elements of $C_s(M)$ results in the reduction of the α irreducible representation of G_{12} :

$$\Gamma_\alpha(G_{12}) = a_{A'}^\alpha A' \oplus a_{A''}^\alpha A'' \quad (4)$$

Applying Eqs. (3) and (4) for all 6 irreducible representations of G_{12} generates the correlation table (Table 4). In the situation where tunneling is feasible, and we wish to label the energy levels resulting from the observable splittings, we want to determine the reverse correlation. The reverse correlation can be determined from the correlation table using the formula [23,24]:

$$\Gamma(\Gamma_i) = \sum_\alpha a_i^\alpha \Gamma_\alpha \quad (5)$$

where $\Gamma(\Gamma_i)$ is the representation induced in G_{12} for the i th irreducible representation in $C_s(M)$. The sum is over all the irreducible representations in G_{12} , with the coefficients a_i^α coming from Eq. (3). The reverse correlation for the two irreducible representations in C_s is obtained by going down the two columns of the correlation table. For the ground state $C_6D_6H^+$ ion, each of these columns represents the reverse correlation for a particular $\Gamma_{J_{KaKc}}$. The resulting sum of all the a_i^α for a single column indicates how many times that particular rotational level is split by tunneling. Application of the reverse correlation, and connection of the symmetry of the asymmetric top wavefunctions is shown in Table 5. The correlation table (Table 4) and the reverse correlation table (Table 5) show that the ground state rotational levels of the rigid ion are split into four tunneling levels in the case of the non-rigid ion.

The induced representation from the reverse correlation only indicates the maximum number of times that an energy level may split in the non-rigid case. Not all of these wavefunctions with the given symmetries will combine with the rotational and nuclear spin wavefunctions to yield an overall molecular wavefunction that satisfies the appropriate Fermi–Dirac and Bose–Einstein statistics. In particular, the overall wavefunction must have a

Table 4
Correlation table between G_{12} and $C_s(M)$.

	A'	A''
A_1	1	0
A_2	0	1
B_1	1	0
B_2	0	1
E_1	1	1
E_2	1	1

Table 5

Application of the reverse correlation to show the splitting of individual asymmetric top rotational energy levels for a $C_6D_6H^+$ in its ground electronic and vibrational state.

$\Gamma_{J_{KaKc}}$	$C_s(M)$	G_{12}
$\Gamma_{J_{ee}}, \Gamma_{J_{oo}}$	A'	$A_1 \oplus B_1 \oplus E_1 \oplus E_2$
$\Gamma_{J_{eo}}, \Gamma_{J_{oe}}$	A''	$A_2 \oplus B_2 \oplus E_1 \oplus E_2$

Table 6

Multiplication of Γ_{tunn} by Γ_r . Γ_r is the symmetry label for the asymmetric top wavefunction J_{KaKc} in the G_{12} MS group.

	Γ_r	Γ_{tunn}	$\Gamma_r \otimes \Gamma_{tunn}$
$\Gamma_{J_{ee}}$	A_1	$A_1 \oplus B_1 \oplus E_1 \oplus E_2$	$A_1 \oplus B_1 \oplus E_1 \oplus E_2$
$\Gamma_{J_{eo}}$	B_2	$A_1 \oplus B_1 \oplus E_1 \oplus E_2$	$B_2 \oplus A_2 \oplus E_2 \oplus E_1$
$\Gamma_{J_{oe}}$	A_2	$A_1 \oplus B_1 \oplus E_1 \oplus E_2$	$A_2 \oplus B_2 \oplus E_2 \oplus E_1$
$\Gamma_{J_{oo}}$	B_1	$A_1 \oplus B_1 \oplus E_1 \oplus E_2$	$B_1 \oplus A_1 \oplus E_1 \oplus E_2$

character of -1 for each permutation of a pair of hydrogen nuclei, and $+1$ for each permutation of a pair of carbon (^{12}C) nuclei. This restriction can be represented as:

$$\Gamma_{rve} \otimes \Gamma_{ns} \supset \Gamma_{Pauli} \quad (6)$$

where Γ_{rve} is the rovibronic symmetry label, Γ_{ns} is that of the nuclear spin wavefunction, and Γ_{Pauli} represents the allowed representations of the overall wavefunction. The term Γ_{rve} can be reduced to Γ_r , because the ground electronic and vibrational state are totally symmetric for the ion. For Γ_r , we are considering the reverse correlation terms from the induced representation of the symmetry labels of the rotational wavefunctions in the rigid case.

The irreducible representations of Γ_{ns} can be found by decomposing the reducible representation formed by computing the total characters of the nuclear spin wavefunctions with the formula [23]:

$$\chi_{ns}^{tot}[P] = \prod_a (2I_a + 1) \quad (7)$$

where the product is taken for each set of nuclei with nuclear spin I_a . For $C_6D_6H^+$ we only have two sets of identical nuclei to consider. All the carbon nuclei are spin-0 bosons, and do not affect the analysis. All the deuterons are spin-1 bosons, while the proton is a spin-1/2 fermion. Application of Eq. (7) yields characters (in G_{12}) of $\chi_{ns}^{tot} = \{1458, 6, 18, 54, 162, 54\}$, which can be decomposed to: $\Gamma_{ns} = 184 A_1 \oplus 76 A_2 \oplus 146 B_1 \oplus 92 B_2 \oplus 232 E_1 \oplus 248 E_2$. Next, the appropriate rotational symmetry species must be matched with the appropriate nuclear spin state species such that spin statistics are obeyed. For $C_6D_6H^+$, all the permutation operations involve bosons, so the overall wavefunction must have a $+1$ character for $E_1(123456)(1'2'3'4'5'6'), (135)(246)(1'3'5')(2'4'6')$, and $(14)(25)(36)(1'4')(2'5')(3'6')$. Thus, the overall wavefunction must belong to the A_1 or A_2 representations in G_{12} . The resulting spin statistical weights for the four split levels of $\Gamma_{J_{ee}}$ and $\Gamma_{J_{oo}}$ is 260:238:464:496 ($A_1:B_1:E_1:E_2$), or roughly 1:1:2:2. This is the same result that can be found for evaluating $\Gamma_{J_{eo}}$ and $\Gamma_{J_{oe}}$.

The process of determining the statistical weights can be simplified by using the following formula [23]:

$$\chi_{rve}^{SW}[P] = 2 \prod_a (2I_a + 1) (-1)^{(2I_a)(n_a - 1)} \quad (8)$$

where χ_{rve}^{SW} is the character of permutation operation P for the spin statistical weight representation of the rovibronic state (Γ_{rve}^{SW}). The χ_{rve}^{SW} for a given permutation operation in the molecular symmetry group is derived from the product of each n_a set of permuted nuclei with spin I_a . The character for any permutation-inversion operation for the group is 0. Application of this formula to the non-rigid

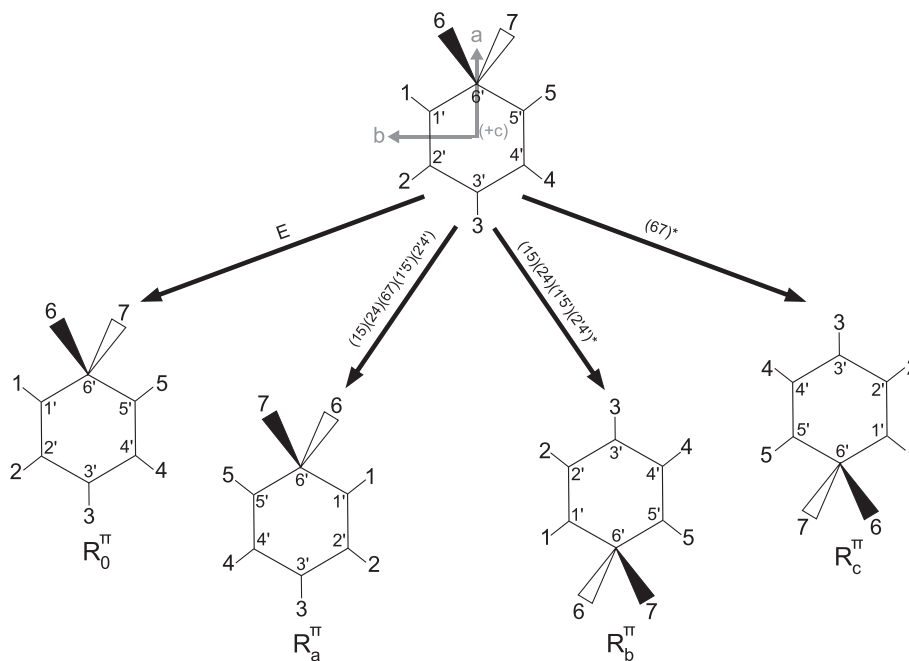


Fig. 4. The four feasible operations in the molecular symmetry group for the rigid benzenium ion. The hydrogen nuclei are labeled 1–7, and the carbon nuclei are labeled 1'–6'. Along each arrow the feasible PI operation is listed. The equivalent rotation corresponding to each feasible operation is listed below the benzenium ion structure that results from each PI operation.

$C_6D_6H^+$ is equivalent to determining Γ_{ns} , and then multiplying it by Γ_{rot} and sorting out the terms that obey the proper spin statistical restrictions.

While MS group theory can indicate the number of levels that result from tunneling, it provides no information about the separation between these tunneling levels. However, there is a simple method that can provide a qualitative estimate of the pattern of the tunneling split levels. This method, developed by Wales [21], is analogous to the linear combination of atomic orbitals (LCAO) method. The LCLW method is also similar to the treatment of n interconnected identical cyclic potential wells, as presented by Hougen et al. [25] for addressing internal rotation problems.

Treating the tunneling problem using the LCLW method is as follows: For a given rovibrational state of a molecule there will be n degenerate minima on the potential energy surface, where $n = h_{CNPI}/h_{rigid}$ is equal to the order of the complete nuclear permutation inversion group for the molecule, divided by the order of the rigid molecular symmetry group [26]. Associated with each of these n degenerate minima is a localized wavefunction where the system is confined to that minimum. A feasible tunneling pathway provides a mechanism that connects a subset of these minima, and the true wavefunctions resulting from the tunneling can be constructed as a linear combination of the localized wavefunctions (LCLW). The number of connected minima $n_{conn} = h_{MS}/h_{PG}$, where h_{MS} is the order of the molecular symmetry group and h_{PG} is the order of the rigid molecule's point group [27].

The problem then reduces to that of a secular determinant, requiring the diagonalization of a $n_{conn} \times n_{conn}$ connectivity matrix, the rows and columns of which represent the connected localized wavefunctions. The diagonal terms of the matrix represent the overall energy of the (unsplit) level, and can be set to zero for convenience. The off-diagonal terms represent the tunneling matrix elements, and are non-zero only for minima that are directly connected by one application of the feasible tunneling pathway. Diagonalization of this symmetric matrix will yield the eigenvalues (relative to the unsplit level) of the tunneling split levels, as well as the eigenvectors which represent the delocalized wavefunc-

tions. The matrix representation of the operators of the non-rigid MS group can be applied to the eigenvectors, permitting symmetry labels to be attached to the corresponding eigenvalues for the splitting energies. These tunneling wavefunctions can be subjected to the spin-statistical restriction of:

$$\Gamma_r \otimes \Gamma_{tunn} \otimes \Gamma_{ns} \supset \Gamma_{Pauli} \quad (9)$$

where Γ_r is the symmetry of the asymmetric top wavefunctions in the non-rigid MS group, Γ_{tunn} is the sum of irreducible representations in the non-rigid group belonging to the LCLWs, and Γ_{ns} is that of the nuclear spin wavefunction. This expression is different from Eq. (6), because one of the normal modes of the ion is being treated as the tunneling pathway, and not considered to be in the ground state. The results of applying Eq. (9) will yield the same number of allowed splittings as found in Eq. (6), and this is shown in Table 6.

Application of the LCLW to describe the tunneling pattern of $C_6D_6H^+$ is completely analogous to the LCAO treatment of the benzene molecule. There are six potential minima connected by the feasible tunneling motion, which is analogous to the case of six carbon atoms contributing a single π electron in the LCAO molecular orbital treatment. The resulting eigenvalues are: $\alpha+2\beta$, $\alpha+\beta$, $\alpha+\beta$, $\alpha-\beta$, $\alpha-\beta$, and $\alpha-2\beta$, where α is the energy of the unsplit level and β is the tunneling splitting, which we have estimated to be ~ 6 MHz using the WKB approximation. The maximum splitting induced by the 1,2-H shift is therefore estimated to be ~ 24 MHz for the $C_6D_6H^+$ in the vibrational ground state.

Using the PI operations in the group, it was possible to also determine the symmetry of the eigenvectors associated with the LCLW eigenvalues. The $\alpha+2\beta$ and $\alpha-2\beta$ levels belong to the one dimensional representations A_1 and B_1 respectively. The doubly degenerate levels $\alpha+\beta$ and $\alpha-\beta$ belong to E_1 and E_2 respectively. Γ_{tunn} therefore spans $A_1 \oplus B_1 \oplus E_1 \oplus E_2$. Γ_{tunn} can be multiplied by the Γ_r symmetry labels for the asymmetric top wavefunctions in G_{12} , shown in Table 3. The result matches that of the reverse correlation table (Table 5), and reveals that all four of the split levels will be allowed for $C_6D_6H^+$.

3. The rigid and non-rigid benzenium ion

In this section, we first start by treating the rigid benzenium ion, and then advance to treating the non-rigid benzenium ion when considering the proton “ring-walk” pathway to be feasible. In Fig. 4 the four feasible operations for the rigid ion are presented. From this set of feasible operations the MS character table (Table 7) is generated. The rigid MS group is isomorphic with the point group C_{2v} . The results of applying the asymmetric top rule to the equivalent rotations in Table 7 is shown in Table 8.

We now consider the non-rigid benzenium ion, in the presence of proton tunneling. As considered for $C_6D_6H^+$, this is the scenario if there is sufficient experimental resolution to observe the result of quantum mechanical tunneling between degenerate equilibrium structures separated by potential energy barriers. This scenario seems likely, given that scrambling of the hydrogen atoms around the ring has been observed experimentally [2,3,8].

The proposed proton “ring-walk” pathway is the same as that presented for $C_6D_6H^+$ on the right hand side of Fig. 3. However, in this case all the tunneling nuclei are now protons, and any individual proton can walk on either side of the carbon ring. The (123456)(1'2'3'4'5'6') feasible “ring-walk” PI operation, along with (15)(1'5')(24)(2'4')(67) [$\sim R_a^\pi$] and (67)* [$\sim R_c^\pi$], can be used as generators to create the entire MS group. To aid in this process, we used the Groups, Algorithms, and Programming (GAP) computational program [28], as demonstrated by Lehmann and Schmieid [29] for generating the character tables and calculating the statistical weights for van der Waals complexes.

Application of GAP generated a molecular symmetry group for the non-rigid benzenium ion of order 60 480 ($G_{60\ 480}$), with 90 irreducible representations and classes of PI group operators. The character table for $G_{60\ 480}$ is not shown here due to its sheer size, but is provided in the Supplementary information.

We now aim to determine how many times an asymmetric top level in the ground electronic and vibrational state for the rigid ion will split due to the “ring-walk” tunneling motion. To do this we generate the correlation table for the $C_{2v}(M)$ MS group into $G_{60\ 480}$ by applying Eqs. (3) and (4) for all four of the irreducible representations in $C_{2v}(M)$. The resulting $G_{60\ 480}$ to $C_{2v}(M)$ correlation table is provided as Supplementary information. The reverse correlation for each of the 4 induced representations into $G_{60\ 480}$ can then be found going down the columns of the correlation table. Application of Eq. (5) to the correlation table reveals that each of the asymmetric top symmetry labels from $C_{2v}(M)$ induce a repre-

Table 7
 $C_{2v}(M)$ character table for the rigid benzenium ion that includes the corresponding equivalent rotations and point group operations.

$C_{2v}(M)$	E	(15)(24)(67)(1'5')(2' 4')	(15)(24)(1'5')(2'4')*	(67)*
Order	1	1	1	1
C_{2v}	E	C_{2a}	σ_{ac}	σ_{ab}
Equiv. rot.	R_0	R_a^π	R_b^π	R_c^π
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Table 8
Application of asymmetric top rule to the rigid benzenium ion.

J_{KaKc}	R_a^π	R_b^π	R_c^π	Γ_{rot}
J_{ee}	+1	+1	+1	A_1
J_{eo}	+1	-1	-1	A_2
J_{oe}	-1	-1	+1	B_2
J_{oo}	-1	+1	-1	B_1

sentation in $G_{60\ 480}$ that corresponds to 464 irreducible representations of $G_{60\ 480}$. This means each rotational level in the ground state could be split into 464 sub-levels by the “ring-walk” tunneling motion.

To determine the total number of allowed tunneling split levels, the restriction of Eq. (6) must be accounted for. The irreducible representations of Γ_{ns} for the non-rigid benzenium ion can be found by using Eq. (7). The Γ_{ns} was found to be composed of 20 irreducible representations, with none higher than 14 dimensional. The product of Γ_r with Γ_{ns} , and applying the restriction of Eq. (6), revealed that a majority of the 464 tunneling levels are forbidden. Qualitatively, this can be understood because a majority of the irreducible representations in the reverse correlation are of higher dimension than 14, and no product between two irreducible representations that are not of the same dimension results in a decomposition that contains a one-dimensional representation. As a result, the rigid rotational levels $\Gamma_{ee}(A_1)$ and $\Gamma_{eo}(A_2)$ will split into 16 allowed levels (not 464), while $\Gamma_{oe}(B_2)$ and $\Gamma_{oo}(B_1)$ will split into 19 levels.

The LCLW method can be used to determine the qualitative pattern of the tunneling splittings in the non-rigid benzenium ion, however, this is a computationally challenging problem. The complete nuclear permutation inversion group of the benzenium ion is $S_7^* \otimes S_6$, and thus the potential energy surface has 1 814 000 ($(h_{CNPI}/h_{C_{2v}} = 7! \times 6! \times 2/4)$) equivalent potential minima. However, only 15 120 ($(h_{MS}/h_{PG} = 60\ 840/4)$) of these are connected; inspection of Fig. 3 shows that the feasible tunneling pathway from a given minimum connects to exactly four other equivalent minima, corresponding to either the top or bottom proton walking one step either clockwise or counterclockwise around the ring.

Moving forward with the LCLW method described by Wales, we have diagonalized the 15 120 \times 15 120 connectivity matrix. Because it was only necessary to consider one tunneling pathway in this problem, the non-zero off-diagonal matrix elements were taken to be unity. The resulting eigenvalues can then be scaled using the tunneling splitting calculated by the WKB approximation in Eq. (2). The matrix diagonalization yielded 392 numerically distinct eigenvalues, with degeneracies corresponding to the assignment of eigenvalues to more than one irreducible representation. Because of the computational expense, the eigenvectors for the eigenvalues were not obtained in the diagonalization of the connectivity matrix. Without the eigenvectors, it is not possible to determine the total number of irreducible representations from the LCLW treatment, or the number of allowed tunneling split levels through application of Eq. (9). The eigenvalues from the diagonalization span values from -4β to $+4\beta$. Using the ~ 6 MHz WKB value for the proton tunneling, this corresponds to a total possible splitting of the rigid level spanning 48 MHz.

4. Conclusions

$C_6D_6H^+$ has served as a test case for the full treatment of the benzenium ion using PI group theory and the LCLW method. Because of the increased mass of the deuteron, it was possible to neglect the 1,2-D shift, and this “trapped” the proton on one side of the carbon ring. Such a simplification leads to a small non-rigid MS group of order 12 (G_{12}), and an LCLW treatment that only involves six equivalent potential minima connected by the feasible tunneling pathway. The correlation table between the rigid and non-rigid MS groups was constructed, and application of the reverse correlation relationship and spin statistical restrictions revealed that each ground state rotational level will be split into four different levels by proton tunneling. To obtain a qualitative estimate of the resulting structure from the tunnel splitting of a ground state rotational level, it was possible to apply the full LCLW

treatment to the $C_6D_6H^+$ ion. The results obtained are analogous to those resulting from the application of Hückel theory to benzene, and agreed with the number of tunneling splittings predicted by the group theoretical analysis.

After developing the application of group theory and the LCLW method to the test case of $C_6D_6H^+$, it was possible to extend these treatments to the complicated case of the non-rigid benzenium ion. The correlation table was constructed between $G_{60/480}$ and $C_{2v}(M)$, and the reverse correlation was determined for the four induced representations belonging to the asymmetric top wavefunctions. The reverse correlation results, when combined with the appropriate spin statistical restrictions, predicted a total number of allowed split levels on the basis of symmetry of 16 for J_{ee} and J_{eo} asymmetric top wavefunctions, and 19 for the J_{oe} and J_{oo} asymmetric top wavefunctions. To obtain a qualitative sense of the magnitude of the energy separation of the ground state energy levels split by the tunneling pathway, the connectivity matrix for the LCLW problem was constructed and diagonalized. Because of the sheer computational expense, the eigenvectors were not obtained from the matrix diagonalization, therefore it was not possible to obtain a qualitative picture of the structure of the tunneling split levels. In the future, we hope to obtain the eigenvectors from the diagonalization of the connectivity matrix in order to enable a prediction of the structure of the tunneling split levels.

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Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University

Molecular Spectroscopy Archives (http://library.osu.edu/sites/msa/jmsa_hp.htm). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jms.2011.04.015](https://doi.org/10.1016/j.jms.2011.04.015).

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