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Geometric phase effect in the vibrational states of triplet H_3^+

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We report calculations of all vibrational states of H_3^+ in the lowest triplet state with the inclusion of the geometric phase effect. When compared with calculations without inclusion of the geometric phase, the results show that only the E' vibrational states are affected, leading to considerable shifts in the vibrational levels and changes in the splittings between the A' and E' levels. The vibrational spectrum of the heavier isotopolog D_3^+ is also analyzed.

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I. INTRODUCTION

It is well-known that conical intersections play a key role in the dynamics of chemical reactions. They occur whenever two electronic states touch each other and originate a breakdown of the standard adiabatic separation between electronic and nuclear motions [1]. The connection of different electronic states through conical intersections allows the occurrence of radiationless decay and charge transfer processes, whose importance is inversely related to the difference between the energy of the system and of the crossing seam. Another phenomenon due to conical intersections is the so-called geometric phase (GP) effect. As shown by Herzberg and Longuet-Higgins [2], a real electronic wave function changes sign when traversing adiabatically a nuclear path that encircles the locus of degeneracy, causing the total wave function to be double-valued, and therefore not well-behaved. In 1984, Berry [3] demonstrated the GP effect (also known as the Berry phase effect or molecular Aharonov-Bohm effect [4]) in a wider context by showing that it can be present on the adiabatic evolution of other quantum systems. In addition to the time-dependent dynamical phase of the wave function, Berry has shown that a cyclic evolution of the parameters of the Hamiltonian (the positions of the nuclei) can make the electronic wave function acquire a phase that depends only on the geometry of the circuit in parameter space (hence the name geometric phase). Thus, such a phase contains information about the past environments of the system, which Berry considered a kind of quantum "memory" [5].

The GP effect arising in the adiabatic evolution of quantum systems has been the subject of much recent investigations [6–10]. Due to its nature, it manifests even if the system is far from the conical intersection. Thus the total electronuclear wave function must be made single valued. To achieve this, one can enforce a sign change in the nuclear wave function by changing from integer to half-odd integer the quantization of the pseudorotation motion around the intersection [11]. Alternatively, one may introduce a vector potential into the nuclear Hamiltonian [12,13]. For a X_3 molecule, one multiplies in the former case the real double-valued electronic wave function by a complex phase factor that changes sign on encircling the conical intersection. Such a complex phase factor originates the vector potential. Conversely, one may introduce the sign change into the nuclear wave function [14]. This can be done by adopting hyperspherical coordinates, since in this coordinate system the GP effect concerns only the ϕ hyperangle associated to the motion around the (single) D_{3h} conical intersection. Being adiabatic in nature, the calculations accounting for the above topological effect involve a single potential sheet and hence differ from the exact nonadiabatic treatment that includes the multiple(two)-sheeted manifold.

A great deal of investigation of the GP effect in molecules has been done in Jahn-Teller systems [9,10,15]. In a typical $E\otimes e$ system, the GP effect has a pronounced impact in the resonance states of the upper excited state, as pseudorotation around the conical intersection is energetically accessible [16,17]. The GP effect in these cone states has been thoroughly investigated in several molecular systems, such as metal trimers, H_3 and H_3^+. As far as the ground state of these Jahn-Teller systems is concerned, the grand candidate for experimental and theoretical studies has always been the H_3 molecule, namely the simple benchmark reaction $H+H_2 \rightarrow H_2+H$. The conical intersection in the H_3 potential energy surface (PES) is about 2.7 eV above the asymptote, making it difficult to reach in most scattering experiments [18]. However, a closed path around this D_{3h} crossing seam is energetically accessible, and so the GP effect is present. In order to clarify its impact in the $H+H_2$ reactive scattering calculations, a series of studies took place in the 1990s, leading to contradictory results. This subject has recently been revisited [19] with a new insight on the problem; the reader is addressed to this work for details.

The GP effect is known to play a special role in the vibronic levels of the lowest adiabatic sheet of $E\otimes e$ Jahn-Teller systems. Its most common effect manifests in the change of order of the lowest levels of the system, with the sequence of such levels changing from $A_1, E, \ldots$ (without GP or NGP) to $E, A_{1(2)}, \ldots$ (GP) [20,21].

The hydrogen molecular ion H_3^+ is of fundamental importance not only because of its simplicity, but also due to its role in astrophysics and astrochemistry. Since it is the lightest triatomic molecule with only two electrons, many of its calculated rovibronic term values for the electronic ground state are known to about spectroscopic accuracy. This has become possible due to sophisticated theoretical methods for

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the calculation of both the electronic energy and the corresponding rovibrational states. Transitions involving the electronic triplet state are believed to be the source of some of the yet unassigned lines observed in hydrogen plasmas, and so accurate calculations of such states are important. The vibrational spectrum of the lowest triplet state of $H_3{}^+$ has already been calculated [22–24], but the GP effect has always been discarded as it was found [22] to be negligible for the lowest states. We now report all vibrational levels of $H_3{}^+(a\,{}^3\Sigma_u^+)$ calculated with the correct boundary conditions.

II. THEORY

The lowest electronic triplet state is Jahn-Teller unstable, and therefore in a displaced nuclear configuration with lower than D_{3h} point group symmetry the PES is split into a lower sheet, $a\,{}^3\Sigma_u^+$, and an upper sheet that resembles an upright cone. At symmetric equilateral arrangements, much above the dissociation of the lower sheet, there is a conical intersection that links the two electronic states. In this lowest electronic triplet state, $H_3{}^+$ is linear, with three equivalent minima (I, II, and III) in the PES, which correspond to the three possible permutations of the nuclei. The three equivalent nuclear arrangements lead to a triplication of the vibrational levels. Due to the barriers between the equivalent minima on the PES, each state becomes split into a singly and a twofold degenerate component. The true wave functions must therefore be a superposition of localized functions $|\Psi^\pm\rangle$.

As a result we obtain the one-dimensional representation

$$|\Psi_A^\pm\rangle \sim |\Psi_I^\pm\rangle + |\Psi_{II}^\pm\rangle + |\Psi_{III}^\pm\rangle \tag{1}$$

and the two-dimensional representation

$$|\Psi_{E,\xi}^\pm\rangle \sim |\Psi_I^\pm\rangle + \omega|\Psi_{II}^\pm\rangle + \omega^2|\Psi_{III}^\pm\rangle, \tag{2}$$

$$|\Psi_{E,\eta}^\pm\rangle \sim |\Psi_I^\pm\rangle + \omega^2|\Psi_{II}^\pm\rangle + \omega|\Psi_{III}^\pm\rangle \tag{3}$$

with $\omega = e^{2\pi i/3}$. The two components of the two-dimensional representation are related by complex conjugation [16].

The $H_3{}^+$ bound states can therefore be classified according to the three-particle permutation inversion group $\mathcal{S}_3 \times I$ [26] which is its molecular symmetry group $D_{3h}(M)$. The symmetry of the total wave functions assumes therefore the form of a direct product of its nuclear spin, rotational, vibrational, and electronic parts,

$$\Gamma_{\mathrm{tot}} = \Gamma_{\mathrm{ns}} \otimes \Gamma_{\mathrm{rot}} \otimes \Gamma_{\mathrm{vib}} \otimes \Gamma_{\mathrm{ele}}. \tag{4}$$

Since for $J=0$, the case of interest in the present work, the rotational wave function is a constant (thus symmetric with respect to the molecular plane), the only irreducible representation of concern here will be A_1'.

For a system of three protons (fermions) the total wave function must be antisymmetric with respect to a permutation of two protons and thus $\Gamma_{\mathrm{tot}} = A_2'$. On the other hand, the electronic symmetry is A_2', and the nuclear spin symmetry is A_1' (E') for the spin quartet (doublet) state. Examination of the direct products of the spin and spatial parts of the total wave function then shows that the physically allowed vibrational wave functions are those of A_1' and E' symmetry, which are to be combined with the quartet nuclear spin function and the doublet nuclear spin function, respectively. A detailed description of the symmetry properties of rovibrational states of $H_3{}^+$ can be found elsewhere [22].

TABLE I. Energies and splittings, in cm^{-1}, of the vibrational states of $H_3{}^+$ without the geometric phase effect (NGP).

i	A_1'	i	A_2'	i	E'	ΔE
0	0.00			0	0.00	0.00
		0	738.48	1	738.48	0.00
1	975.05			2	975.05	0.00
2	1273.81			3	1273.79	0.02
		1	1474.40	4	1474.43	−0.03
3	1573.84			5	1573.80	0.04
		2	1727.77	6	1728.40	−0.63
4	1923.18			7	1923.03	0.15
5	1955.25			8	1950.94	4.31
		3	1969.54	9	1970.69	−1.15
		4	2127.70	10	2136.88	−9.18
6	2168.04			11	2166.38	1.66
		5	2247.36	12	2250.97	−3.61
7	2269.28			13	2259.30	9.98
8	2348.36			14	2334.96	13.40
		6	2350.99	15	2356.74	−5.75
		7	2368.01	16	2359.63	8.38
9	2397.61			17	2402.06	−4.45
		8	2404.21	18	2410.28	−6.07
		9	2415.75	19	2427.86	−12.11
10	2423.79			20	2431.27	−7.48

The vibrational bound states have been obtained by solving the time-independent Schrödinger equation with the Hamiltonian written in modified hyperspherical coordinates and neglecting spin-orbit and spin-spin interactions [25]. This method employs symmetry adapted basis functions that allow us to assign the calculated bound states to the irreducible representations mentioned above. The action of the Hamiltonian on the wave function (Lanczos vector) has been carried out using a mixed grid-basis method and the recursion Lanczos algorithm [25]. The results obtained are significant, as knowledge of the $H_3{}^+$ spectroscopy is required with high accuracy, both theoretically and experimentally. Thus any changes in the vibrational spectrum due to the inclusion of the GP effect should be reported.

III. RESULTS AND DISCUSSION

Tables I and II show the vibrational levels calculated up to the zero point energy (ZPE) of $H_2{}^+(X\,{}^2\Sigma_g^+)$ (2431.30 cm^{-1} above the first vibrational level of $H_3{}^+$ and 13 727.63 cm^{-1} below the minimum of the conical intersection), together with the splittings between the singly and twofold components. In the $H_3{}^+(a\,{}^3\Sigma_u^+)$ system studied in the present work, tunneling is not sufficiently effective to split the first three

TABLE II. Energies and splittings, in cm^{-1}, of the vibrational states of $H_3{}^+$ with the geometric phase effect (GP).

i	A_1'	i	A_2'	i	E'	ΔE
0	0.00			0	0.00	0.00
		0	738.48	1	738.49	−0.01
1	975.05			2	975.05	0.00
2	1273.81			3	1273.75	0.06
		1	1474.40	4	1474.48	−0.08
3	1573.84			5	1573.72	0.12
		2	1727.77	6	1729.69	−1.92
4	1923.18			7	1922.71	0.47
5	1955.25			8	1943.61	11.64
		3	1969.54	9	1972.17	−2.63
		4	2127.70	10	2156.40	−28.70
6	2168.04			11	2167.49	0.55
		5	2247.36	12	2230.63	16.73
7	2269.28			13	2263.87	5.41
8	2348.36			14	2317.85	30.51
		6	2350.99	15	2344.51	6.48
		7	2368.01	16	2367.33	0.68
9	2397.61			17	2402.63	−5.02
		8	2404.21	18	2414.86	−10.65
		9	2415.75	19	2449.09	−33.34
10	2423.79			20	2456.83	−33.04

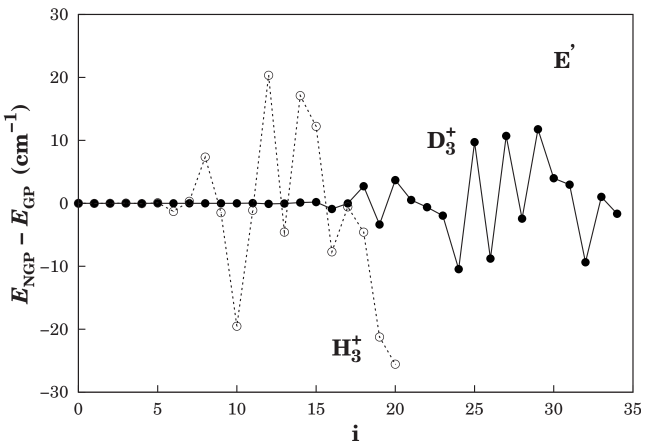

FIG. 1. Energy differences, in cm^{-1}, of the NGP and GP E' levels of $H_3{}^+$ (presented in Tables I and II) and $D_3{}^+$.

levels, even with the inclusion of the GP effect, and so no reordering of the levels is observed [20,21]. For this reason, all the vibrational levels were calculated with respect to the level $i=0$ (A_1' or E'). The most striking difference between the levels presented in both tables is that all of the A' states remain unchanged in the NGP and GP calculations, even though most of them are higher in energy than the saddle point (pseudorotational barrier), which is 873.69 cm^{-1} above the first vibrational level. This can be explained by the fact that vibronic modes of A' symmetry do not lead to motion encircling the conical intersection and hence are GP inactive. The A' modes are then expected to be localized over the attractive wells even in the case of vibrational states much above the bottom of the PES and close to ZPE of the $H_2{}^+$ fragment. Conversely, the E' modes do contribute to such an encircling motion, with their associated wave functions being delocalized over the attractive wells. As for the E' vibrational levels, their difference in the NGP and GP calculations can be seen in Fig. 1. Up to level $i=7$, the differences are very subtle, revealing the fact that the wave functions of these levels are almost completely localized over the attractive wells. The GP effect in these levels is therefore negligible, as stated in [22]. Above this vibrational level the differences between the two sets start to increase more frequently due to delocalization of the wave functions. In these cases the nuclear probability density becomes nonzero which facilitates pseudorotation (i.e., it is easy to perform a complete rotation along the ϕ hyperangle). The same reasoning can be used to explain the differences between the splittings of both calculations [note that $E_{NGP}(E')-E_{GP}(E') = \Delta E_{GP} - \Delta E_{NGP}$]: the connection of the different minima by the nuclear density probability (wave function squared) indicates a higher probability of tunneling between the three symmetry-related minima when the GP effect is considered.

The increasing delocalization of the wave functions from the NGP to GP calculations can be seen in Fig. 2, where the nuclear probability densities of the first E' level for $Mu_3{}^+$ ($i=0$) with and without inclusion of the GP effect are depicted. Note that we have considered this unusual species for computational reasons, since the desired GP effects only arise in highly vibrational excited states for the heavier isotopologs and hence are difficult to compute accurately by full-diagonalization of the Hamiltonian matrix. Figure 2(a) shows that the three maxima of the nuclear NGP probability density are located over the three equivalent minima of the PES ($\beta^*=0, \gamma^*=1$, and symmetry related positions), with no significant probability density being observed between those minima. This is not the case in Fig. 2(b), where significant nuclear probability density connects the minima in the GP case. Note that the E' wave functions are known to occur in pairs, one of which is shown in Fig. 2. The one shown has a predominant amplitude over one well and a node bisecting the other two wells. Of course, this is easily distinguishable from an A' one in that the latter must have D_{3h} symmetry. However, the important feature is that the density extends over the three wells in the GP case.

Our results are well-converged, with a maximum error norm of 2 cm^{-1} for the states close to dissociation, and <1 cm^{-1} for the lowest states. Because the vibrational levels presented here have been calculated using the PES obtained in [24], we can compare them with the NGP results reported in that work. The largest difference between the two sets of calculations is the total number of levels below the ZPE of $H_2{}^+$, 63 in this work versus the previous 51 levels. Such a disparity can be explained by the different methods used in the calculations. Recall that the method used here [25] utilizes the Lanczos recursion algorithm, which yields a tridiagonal Hamiltonian. This is then diagonalized by the minimum-residual filter diagonalization (MFD) technique [28]. Such a method has proved to be powerful when calculating the high-lying vibrational eigenstates of a molecule,

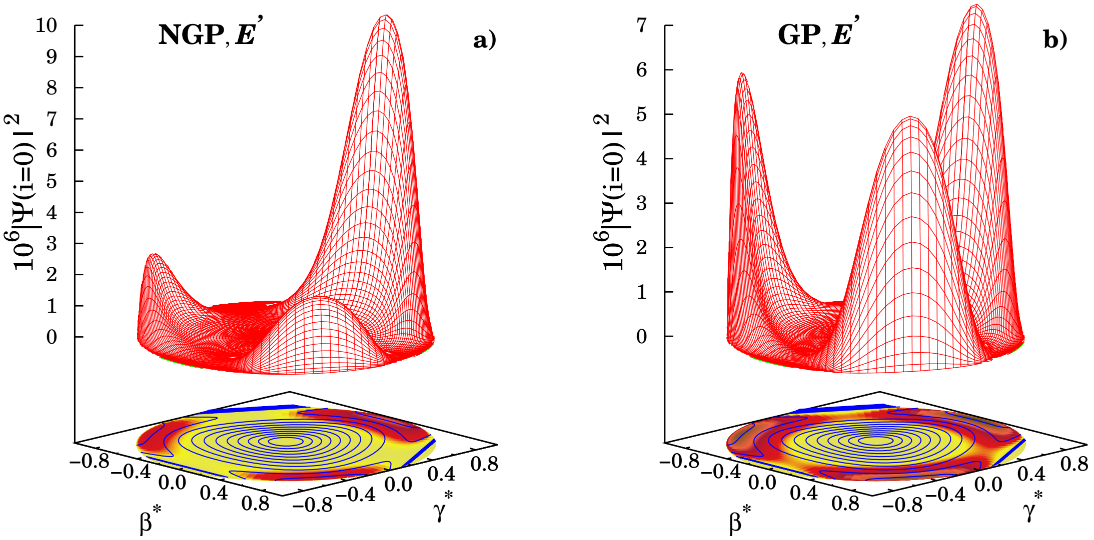

FIG. 2. (Color online) Triangular plot in hyperspherical coordinates of cross sections of the nuclear probability densities with and without consideration of GP effect. The value of ρ is fixed at the value corresponding to the maximum probability density. Contours of the PES are also shown in black (blue in the online version) as a projection in the (β^*, γ^*) space [27].

especially if it is a floppy one. Thus the present results are expected to be more accurate for the higher states than in [24].

We have performed similar calculations on D_3^+. Due to its larger reduced mass, D_3^+ has a smaller ZPE and the PES supports more bound states than H_3^+ (the tables containing the vibrational levels are available from the authors upon request). As expected, the tunneling splitting in D_3^+ decreases when compared to the lighter H_3^+ isotopolog. Moreover, like H_3^+, all vibrational states below the pseudorotational barrier (1370.24 cm^{-1} above ZPE) are nearly degenerate. The GP effect has also no impact on the A' levels, with the differences between the NGP and GP calculations being shown in Fig. 1. In summary, the GP effect has a smaller impact in the D_3^+ spectrum, as it can be seen from Fig. 1. This indicates that the wave functions of the E' levels are less delocalized, and hence pseudorotation will be harder to accomplish.

IV. CONCLUSION

In the present work we have studied the role of the GP effect in the vibrational levels of the lowest adiabatic sheet of triplet H_3^+ and the heavier D_3^+ isotopolog. It is shown that only levels of E' symmetry are altered by this topological effect when compared to NGP calculations. As a result, one observes significant shifts between the NGP and GP E' levels. Corresponding changes are then observed in the splittings between the A' and E' levels when the GP effect is included.

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