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Symmetry Analysis of the Vibronic States in the Upper Conical Potential ($2^3A'$) of Triplet H_3^+

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The symmetry properties of the rovibronic resonance states (Slonczewski resonances) supported by an upright conical potential are investigated. These symmetry properties lead to a useful correlation between states calculated with and without consideration of the geometrical phase, which can assist in the assignment of those states. The vibronic resonance states of triplet H_3^+ ($2^3A'$), which had been studied by us before, have now been assigned to spectroscopic quantum numbers.

1. Introduction

Thirty years ago, Schaad and Hicks,[1] in a systematic study of the excited electronic states of H_3^+, discovered that the lowest electronic triplet state of this molecular ion is bound. Theoretical studies that followed, by Ahlrichs et al.,[2] Wormer and de Groot,[3] and Preiskorn et al.,[4] yielded the equilibrium geometry data, harmonic frequencies, and the first, however incomplete, potential energy surface.[3] It has only been during the past three years, that a number of articles have been published, by the present authors[5−7] and by Sanz et al.,[8,9] that provide complete potential energy surfaces and the first accurate quantitative data on the rovibronic structure of H_3^+ in its lowest triplet state, $a^3\Sigma_u^+$. Triplet H_3^+ is subject to a strong Jahn Teller effect, and the $a^3\Sigma_u^+$ state forms the lower sheet of a double-valued potential energy surface. The upper sheet potential[10] resembles an upright cone at nuclear arrangements close to that of an equilateral triangle, where the two potentials become degenerate.

In recent publications,[6,10,11] we explored the analytical representation of the two sheets by double many-body expansion (DMBE) theory.[12,13] In the most recent of these,[11] an improved representation of the two sheets was obtained, based on an extended set of ab initio electronic energy data and a novel analytical DMBE approach, in which the degeneracy of the two sheets at the conical intersection is guaranteed by construction. In the present paper we report the calculation of the vibronic states in the upper conical potential as predicted from the improved potential energy surface. We have also examined the symmetry properties of these states and assigned them with spectroscopic quantum numbers.

2. Vibronic Cone Sates and Their Symmetry Properties

The vibronic states supported by the conical potential are resonance states, sometimes known as Slonczewski resonances,[14] which decay nonadiabatically to the lower sheet of the potential energy surface. To determine the positions and lifetimes of these resonance states, a vibronic calculation on the two coupled potential energy surfaces would be required. In the present case of triplet H_3^+, however, one should be able to obtain accurate estimates of the resonance positions alone from a single surface calculation. For triplet H_3^+, the conical intersection line appears at energy values high above the $H_3^+(X^2\Sigma_g^+) + H(^2S)$ dissociation threshold of the lower sheet, so that the conical resonance states are embedded in the continuum of the lower sheet. As discussed in ref 10, based on results obtained by one of us and Nikitin,[15] we do not expect such a coupling to continuum states to have a strong influence on the positions of the resonances. To be sure, in such a single surface calculation one must take into account one consequence of the conical intersection, the geometrical phase. Geometrical phase boundary conditions are required for the rovibrational wave functions to counteract the corresponding phase change of the electronic wave function. A rovibrational calculation without geometrical phase boundary conditions (NGP calculation) can nevertheless be useful to assist the assignment of the proper eigenvalues obtained from a calculation that takes into account the geometrical phase (GP calculation), as the two sets of eigenvalues are correlated.

For the calculation of the vibrational states we employed our latest DMBE surface.[11] Two different methods were then used, both based on hyperspherical coordinates, since such coordinates permit an accurate description of pseudorotation. While the NGP calculations were performed with the method of hyperspherical harmonics,[16] the GP calculations were based on the mixed grid basis method described in ref 17. As in our previous calculations, nuclear masses were used as required in the adiabatic separation of nuclear and electronic motions. For a discussion of mass effects see refs 18 and 19 and references therein. The hyperspherical basis functions of the two methods mentioned above can be symmetrized with respect to an exchange of identical nuclei and the inversion of the coordinate system. Thus, the hyperspherical methods allow separate calculations to be carried out for each of the irreducible representations of the three-particle permutation-inversion group[20,21] $S(3) \times I$. This group is isomorphic with the D_{3h} point group and has six irreducible representations. The $J = 0$ functions are symmetric with respect to the inversion of the coordinate system, the remaining irreducible representations being A_1', A_2' and E'. The wave functions of the physically allowed states for a system of three protons (fermions) must be antisymmetric with respect to a permutation of two protons and thus transform as A_2'. In ref 10 we have examined the symmetry properties of the electronic and the nuclear spin parts of the total wave function. The electronic symmetry is A_1', while the nuclear spin symmetry is

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A_1' for the spin quartet state and E' for the spin doublet state. Examination of the direct products of the spin and spatial parts of the total wave function shows that the physically allowed vibrational wave functions are those of A_2' and E' symmetry, which are to be combined with the quartet nuclear spin function and the doublet nuclear spin function, respectively.

In spectroscopic notation, the rovibronic states are represented as linear combinations of

$$|\Psi\rangle = |v_1 v_2 l\rangle\, |Jk\rangle e^{i\alpha\phi} \tag{1}$$

Here, v_1 is the symmetric stretch quantum number, v_2 that of the degenerate vibration, and l the associated vibrational angular momentum which takes the values

$$l = v_2, v_2 - 2, \ldots - v_2 \tag{2}$$

As usual, J is the total angular momentum and k its internal projection. Finally, $e^{i\alpha\phi}$ is the geometrical phase factor, written in its most basic from. For a general discussion of this factor, see ref 22. The electronic spin has been neglected in the above equations. Symmetrization of the primitive basis functions eq 1 leads to the Wang-type linear combinations[23]

$$|\Psi_\pm\rangle = \frac{1}{\sqrt{2}}(|v_1\, v_2, l + \alpha\rangle\, |Jk\rangle \pm (-1)^J |v_1\, v_2, -l - \alpha\rangle\, |J - k\rangle) \tag{3}$$

which are irreducible representations of $S(3) \times I$. If no geometrical phase is present, α takes the value $\alpha = 0$, otherwise it is $\alpha = 1/2$. In the latter case, l is thus replaced by the half integer pseudorotational quantum number[24]

$$|j| = |l| + \frac{1}{2} \tag{4}$$

The symmetry of the vibronic states, i.e., the $J = 0$ states, is determined entirely by the pseudorotational quantum number.[25] In the NGP case, the functions $|\Psi_\pm\rangle$ with $|l| = 0, 3, \ldots$ transform as A_1' and A_2', the others as E'. In the GP case, it is the states with $|j| = 3/2, 9/2, \ldots$ or $2|j| = 3(2i + 1)$, $i = 0, 1, \ldots$ that transform as A_1'/A_2' pairs, while the others transform as E'. If rotation is excited, the quantum numbers l and k are not conserved separately, as shown by Hougen[26] and by Watson.[27] To account for this, they introduced a new good quantum number, $G = |k - l|$. In the presence of a geometrical phase, the corresponding half integer good quantum number becomes[23]

$$G = |k - j| \tag{5}$$

The rovibronic wave functions are eigenfunctions of the parity operator, which leads to the prime or double prime classification. Parity is determined by the parity of k, the projection of the angular momentum operator.[28] The vibronic states considered in the present article obviously have $k = 0$ and thus positive parity. In this case, $G = |j| = |l| + 1/2$. The transformation properties of the functions defined in eq 3 are shown in Table 1. They will form the basis of our assignment procedure.

3. Assignment of the Vibronic Cone States

We will first discuss the case in which the geometrical phase is neglected. With symmetry classification of the spectroscopic states at hand, Table 1, the spectroscopic assignment of the calculated states, Table 2, is now fairly straightforward. Looking at the latter table, we note the absence of states with symmetry A_2'. This shows that there are no states with 3-fold excitation of ν_2 and $|l| = 3$, as such states would form an A_1'/A_2' pair. The states in the A_1' column are thus characterized by $(v_1, v_2^{|l|}) = (v_1, 0^\circ)$ and $(v_1, 2^\circ)$, those of the E' column by $(v_1, 1^1)$, $(v_1, 2^2)$, and possibly $(v_1, 3^1)$. The lowest states in the A_1' column, $i = 0, \ldots 4$, can now be readily assigned to $(v_1 = i, 0^\circ)$. The hyperspherical states $i = 5, 6$ are close in energy, but, judging from the energy differences in the progressions of the lower members, we conclude that it is the state with $i = 5$ that corresponds to $(5, 0^\circ)$. The state with $i = 6$ must belong to a different series, and we assign it to $(0, 2^\circ)$. The higher members of the two families of states, $(v_1, 0^\circ)$ and $(v_1, 2^\circ)$ can now be identified securely, except perhaps for $i = 14$ and $i = 15$, which are separated by only 12 cm^{-1}. Since there is no reason why the two series should cross, we made the assignments as shown in Table 2. Note that all these states are unphysical, since they violate the antisymmetry principle.

TABLE 1: Symmetry Classification of the Spectroscopic Functions[a]

	$(-1)^k = 1$	$(-1)^k = -1$
$G = 0, 3, \ldots$	A_1'/A_2'	A_1''/A_2''
$G = 1, 4, \ldots$	E'	E''
$G = 2, 5, \ldots$	E'	E''
$G = 3/2, 9/2, \ldots$	A_1'/A_2'	A_1''/A_2''
$G = 1/2, 7/2, \ldots$	E'	E''
$G = 5/2, 11/2, \ldots$	E'	E''

[a] Integer values of G, with $\alpha = 0$, correspond to the NGP case, while half integer values of G, with $\alpha = 1/2$, correspond to the GP case.

TABLE 2: Vibronic Energy Values, in cm^{-1}, of the NGP States and Their Assignments[a]

$(v_1, v_2^{\lvert l\rvert})$	$(v_1, v_2^{\lvert l\rvert})$	i	A_1'	i	E'
$(0, 0^0)$		0	3702.78		
$(1, 0^0)$		1	4357.46		
$(2, 0^0)$		2	4966.61		
	$(0, 1^1)$			0	5515.15
$(3, 0^0)$		3	5526.50		
$(4, 0^0)$		4	6032.78		
	$(1, 1^1)$			1	6036.70
$(5, 0^0)$		5	6480.16		
	$(2, 1^1)$			2	6499.91
$(0, 2^0)$		6	6568.21		
	$(0, 2^2)$			3	6771.02
$(6, 0^0)$		7	6862.19		
	$(3, 1^1)$			4	6896.82
$(1, 2^0)$		8	6964.81		
	$(1, 2^2)$			5	7144.82
$(7, 0^0)$		9	7170.84		
	$(4, 1^1)$			6	7216.75
$(2, 2^0)$		10	7280.04		
$(8, 0^0)$		11	7396.62		
	$(2, 2^2)$			7	7413.77
	$(5, 1^1)$			8	7434.22
	$(0, 3^1)$			9	7448.06
$(3, 2^0)$		12	7493.15		
$(9, 0^0)$		13	7534.01		
	$(3, 2^2)$			10	7553.77
$(4, 2^0)$		14	7574.25		
$(10, 0^0)$		15	7586.68		
	$(6, 1^1)$			11	7587.86

[a] Data are with respect to the potential minimum.

The states of E' symmetry, which are physically allowed, are now assigned with the same strategy. Identifying the three lowest hyperspherical states without problem to $(v_1, 1^1)$, $v_1 = 0, 1, 2$ and observing their energy differences, we find that $i = 3$ must belong to a new family and thus assign it as $(0, 2^2)$. We now easily follow the vibrational stacks of the two families, $(v_1, 1^1)$ and $(v_1, 2^2)$, until we find three states close in energy, $i = 7, 8,$

9, one of which must belong to a new family. With careful consideration this state is identified as $i = 9$, and we assign it as $(0, 3^1)$.

The algorithm applied here for the assignment of the vibrational states is a simplified version of the more general algorithm for the semiautomatic assignment of rovibrational states developed by one of us,[29] which has been applied to H_3^+ and its isotopomers in the electronic ground state[19,30−33] and to H_3^+ in the lowest triplet state,[7] $a^3\Sigma_u^+$. It is based on the exact symmetry, i.e., permutation inversion symmetry, of the spectroscopic states and on the recognition of vibrational and rotational progression patterns and has been developed to permit assignments when wave functions are not easily accessible, as it is the case in our present implementation of the hyperspherical harmonics method. Note that no fit to energy eigenvalues of a phenomenological Hamiltonian is required. This is a useful feature, as frequently such phenomenological expansions converge only slowly. In the present case, it is possible to fit the vibrational stretch progressions of each (v_2, l) family separately if the lowest members of the series, which are most strongly affected by the conical intersection, are excluded. The expansion in terms of the quantum number v_1 is then

$$E_{v_2,l}(v_1) = \sum_{i=0} c_{v_2,l,i}\, v_1^i \tag{6}$$

Note that due to the conical behavior of the potential, the zero-point energy cannot be approximated as $E_{v_2,l}(0) \approx 1/2\, \hbar\omega_1$, and a zero-order term is required explicitly in eq 6. Though these fits are not powerful enough to distinguish between close lying states near the dissociation thresholds, they otherwise confirm our assignments. Since all vibrational states up to the dissociation threshold have already been assigned, we do not present the explicit values of the expansion coefficients.

As discussed above, the NGP states presented in Table 2 have no physical meaning, since they were calculated with inappropriate cyclic boundary conditions. They are nevertheless useful as they can be assigned easily, and with their identification at hand the spectroscopic assignment of the true states, i.e., those calculated with the correct cyclic boundary conditions to ensure the geometrical phase, is facilitated. When the geometrical phase effect is taken into account, the quantum number of the vibrational angular momentum, l, has to be modified to obtain the half integer pseudorotational quantum number[24] $|j| = |l| + 1/2$. The symmetry of the vibronic GP states is determined by this quantum number, as summarized in Table 1.

These symmetry considerations, together with the spectroscopic identification of the NGP states, can now be used to assign the GP states in Table 3. It is now clear that the A_1'/A_2' states must have an odd value of v_2. They are thus derived from the appropriate NGP states of E' symmetry. The spectroscopic labels of the GP states are $(v_1, v_2^{|j|}) = (v_1, 1^{3/2})$ or $(v_1, 3^{3/2})$.

For $i = 0, \ldots 4$, the assignment is straightforward and we obtain $(v_1 = i, 1^{3/2})$. Of the A_1' states with $i = 5$ and $i = 6$, one must be $(5, 1^{3/2})$ and the other $(0, 3^{3/2})$. As they are separated by only 5 cm^{-1}, we cannot assign them uniquely. The assignments that we propose must be understood as tentative assignments. Note that the A_1' states with $i > 4$ lack their A_2' counterparts, as such states would be in the continuum. Judging from the lower members, the splitting between the A_1' and corresponding A_2' states is of the order of 200 cm^{-1}. As in the NGP case, states of A_1' symmetry are unphysical.

While GP states of A_1'/A_2' symmetry arise due to an odd excitation of the degenerate mode ν_2 ($v_2 = 1, 3$), those of E' symmetry have an even excitation ($v_2 = 0, 2$) of this mode. The lowest five E' states are now readily assigned as $(v_1 = i, 0^{1/2})$ with $i = 0, \ldots 4$. By analyzing the energy differences between consecutive states of this family, we can identify the states with $i = 6, 9, 11$ as $v_1 = 5, 6, 7$, respectively. The state with $i = 5$, which was left over, must be the lowest member of a new family, $(0, 2^{1/2})$. Of the states $i = 7$ and $i = 8$ one must be $(1, 2^{1/2})$, the other $(0, 2^{5/2})$. The assignments that we have made for these states seem the most reasonable, since also in the NGP case $(0, 2^2)$ is below $(1, 2^{\circ})$. The assignments that we propose for the remaining states $i = 10, 12, 13$ are based on this choice.

TABLE 3: Vibronic Energy Values, in cm^{-1}, of the GP States and Their Assignments[a]

$(v_1, v_2^{\lvert j\rvert})$	$(v_1, v_2^{\lvert j\rvert})$	i	A_1'	i	A_2'	i	E'
	$(0, 0^{1/2})$					0	4700.90
	$(1, 0^{1/2})$					1	5288.84
	$(2, 0^{1/2})$					2	5826.05
$(0, 1^{3/2})$		0	6106.55				
$(0, 1^{3/2})$				0	6300.74		
	$(3, 0^{1/2})$					3	6307.25
$(1, 1^{3/2})$		1	6562.47				
	$(4, 0^{1/2})$					4	6725.85
$(1, 1^{3/2})$				1	6750.44		
$(2, 1^{3/2})$		2	6950.69				
	$(0, 2^{1/2})$					5	6985.17
	$(5, 0^{1/2})$					6	7073.41
$(2, 1^{3/2})$				2	7129.24		
$(3, 1^{3/2})$		3	7259.31				
	$(0, 2^{5/2})$					7	7297.96
	$(1, 2^{1/2})$					8	7315.96
	$(6, 0^{1/2})$					9	7339.11
$(3, 1^{3/2})$				3	7421.18		
$(4, 1^{3/2})$		4	7470.73				
	$(1, 2^{5/2})$					10	7503.57
	$(7, 0^{1/2})$					11	7519.49
$(0, 3^{3/2})$		5	7559.94				
$(5, 1^{3/2})$		6	7564.94				
	$(2, 2^{1/2})$					12	7574.57
	$(2, 2^{5/2})$					13	7585.88

[a] Data are with respect to the potential minimum.

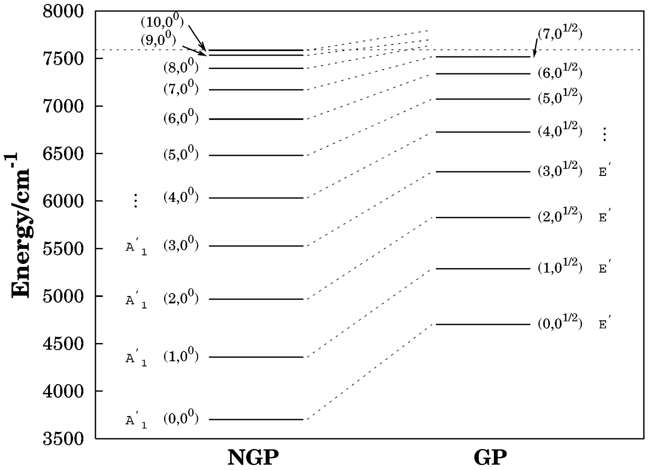

Figure 1. Correlation of the $v_2 = 0$ states calculated without (left) and with (right) inclusion of the geometrical phase. The dissociation energy ($E_{\mathrm{diss}} = 7591.63$ cm^{-1}) is indicated by a broken line.

Our results are displayed graphically in Figures 1−3. These figures show the correlation between the NGP and the GP states for the three families of vibronic states, $(v_1, v_2 = 0)$, $(v_1, v_2 = 1)$, and $(v_1, v_2 = 2)$.

Finally, the eigenvalues of the vibronic states obtained here can be compared with those obtained by us previously[10] on a

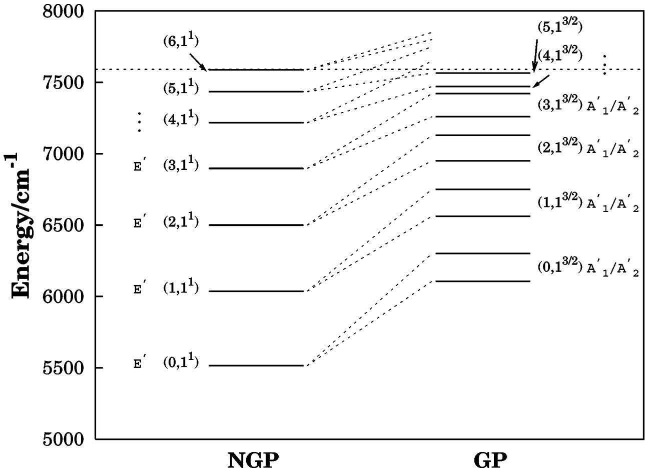

Figure 2. Correlation of the $v_2 = 1$ states calculated without (left) and with (right) inclusion of the geometrical phase. The NGP states have E' symmetry and are split into an A_1'/A_2' pair when the geometrical phase is taken into account.

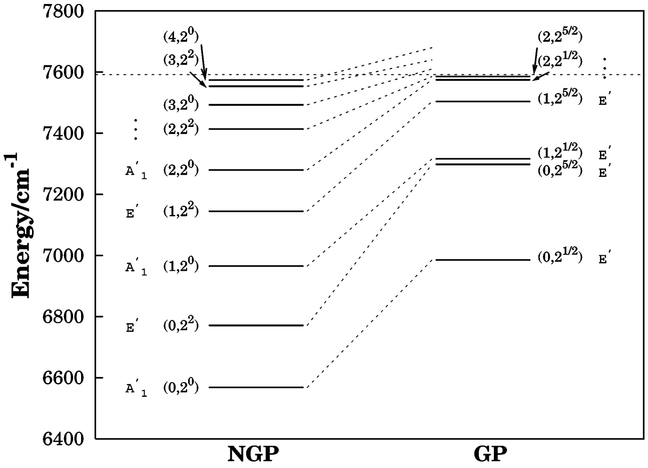

Figure 3. Correlation of the $v_2 = 2$ states calculated without (left) and with (right) inclusion of the geometrical phase. Note the different scale of the ordinate compared with Figures 1 and 2.

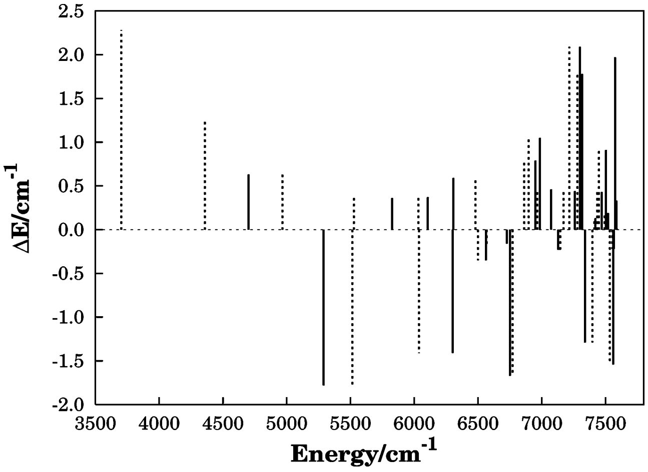

Figure 4. Energy differences $\Delta E = E(\text{ref } 10) - E(\text{this work})$ of the positions of the resonance states calculated using two different potential energy surfaces. The full lines refer to the GP states, while the broken lines refer to the NGP states.

different potential energy surface. Figure 4 shows that the two surfaces are equivalent over the whole energy region. The differences $\Delta E = E(\textit{Ref. } 10) - E(\textit{this work})$ of the calculated vibronic states have a mean value $\bar{\Delta}E = 0.213$ cm^{-1} and a standard deviation $\sigma = 1.077$ cm^{-1}. They are thus well within the error bounds of the fits of the ab initio electronic energy data ($\approx$5.5 cm^{-1}) and are not significant with respect to the accuracy of the electronic energy data themselves.

4. Conclusions

In the present work we have determined the positions of the vibronic resonance states in the upper conical potential of triplet H_3^+, using a new DMBE potential energy surface. The symmetry properties of these states were studied and spectroscopic assignments were made. We plan to develop further our GP computer code to permit calculations for nonzero angular momentum and eventually also to perform coupled surface calculations.

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