An Ab Initio Study of the Vibronic Structure in the $a^1\Delta_g$ Electronic State of $C_2H_2^{++}$

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The results of an ab initio study of the vibronic structure in the $a^1\Delta_g$ electronic state of $C_2H_2^{++}$ and its deuterated species ($C_2D_2^{++}$) are presented. They are generated employing a simple model that incorporates the minimal number of terms contributing to the Renner−Teller effect. The *trans*- and *cis*-bending potential curves at planar nuclear arrangements are obtained by means of large-scale configuration interaction calculations. The corresponding harmonic vibrational frequencies are 717 and 650 cm^{-1} for $C_2H_2^{++}$, and 549 and 477 cm^{-1} in the case of $C_2D_2^{++}$. It is found that the splitting of the potential surfaces is moderate at *trans*-distortions of linearity, while it is extremely small at *cis*-bending vibrations. The eigenvalues and eigenfunctions of the model Hamiltonian employed are obtained by means of a perturbative and a variational approach.

1. Introduction

Previous theoretical and experimental investigations have established that the acetylene dication is a stable species in the microsecond to millisecond time scale.[1−4] It is believed that this metastability is due to the formation, in these experiments, of this dication in its lowest electronic states, namely, the $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$ states. For the upper electronic states, fast dissociation processes and fast dicationic acetylene−vinylidene isomerization phenomena were noticed.

The main aim of the present theoretical contribution is to provide insight into the vibronic structure of the lowest $^1\Delta_g$ state of $C_2H_2^{++}$. The vibronic structure in such a doubly degenerate electronic state is rather complicated because of the Renner−Teller (RT) effect. The RT effect in Δ electronic states of four-atomic molecules has been investigated very rarely. In refs 5−8, a theoretical model for variational and perturbative ab initio handling of this phenomenon has been developed. It was employed in refs 5−8 to compute the vibronic structure in the excited $1^1\Delta_g$ electronic state of B_2H_2. In these studies, the potential energy computations were performed using configuration interaction approaches and large basis sets.

The experimentally resolved spectra treating the *a* state of $C_2H_2^{++}$ consists of a vibrational series that is attributed to the excitation of the ν_2 C−C stretching mode when the dication is obtained by removal of two electrons from the neutral C_2H_2 molecule. The earlier theoretical works by Ohrendorf et al.,[9] Andrews et al.,[10] Thissen et al.,[1] Duflot et al.[2] and, more recently, by Furuhashi et al.[11] and Kinugawa et al.[3] allowed determination of the relative energy of the *a* state with respect to the ground state, the shape of its potential energy surfaces along the stretching coordinates, and its harmonic wavenumbers. However, no information on the bending pattern of the $C_2H_2^{++}$($a^1\Delta_g$) beyond the harmonic approximation is available in the literature. Hence, our computed vibronic spectra of $C_2H_2^{++}$($a^1\Delta_g$) and its deuterated species are predictive in nature and should be helpful in the understating of the corresponding experimentally rovibronic resolved spectra when measured.

2. Technical Details

For molecular dicationic species, only interaction configuration approaches can be used for the calculations of their properties because of their multi-configuration nature. Here the one-dimensional cuts of the 6-D potential energy surfaces of both components of the doubly degenerate $C_2H_2^{++}$($a^1\Delta_g$) along the bending coordinates are computed using such approaches, namely, the complete active space self-consistent field (CASSCF) method[12] followed by the internally contracted multireference configuration interaction (MRCI)[13,14] technique. For these computations, the carbon and the hydrogen atoms were described using the *spdf*(*g*) cc-pV5Z Dunning's basis set.[15] All valence electrons were correlated. All electronic calculations were performed using the MOLPRO program suite.[16] In the CASSCF active space, all valence molecular orbitals were optimized. These calculations were carried out in the C_1 point group. The CASSCF active space comprised all configurations (configuration state functions (CSFs)) obtained after excitations of all valence electrons in valence orbitals. Moreover, three singlet electronic components (two for the $a^1\Delta_g$ and one for the $b^1\Sigma_g^+$) have been averaged together using the CASSCF averaging procedure implemented in MOLPRO. At the MRCI level, all configurations in the CI expansion of the CASSCF wave function were taken into account as a reference, resulting in more than 108×10^6 CSFs to be treated.

The variational and perturbative approaches employed in the present study for calculating vibronic spectra are described in detail elsewhere (see refs 5−8, 17, and 18 and the references therein). In the context of this work, the most important fact is that the model applied does not require calculating the complete four-dimensional potential energy surface involving simultaneous variation of all bending coordinates; it has been shown

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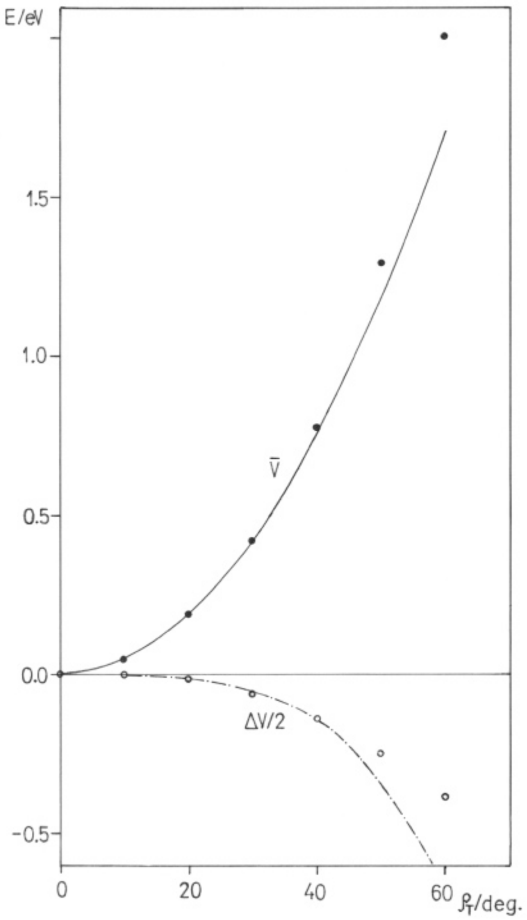

Figure 1. Ab initio computed values for the mean value ($\bar{V}$) of the adiabatic electronic energies for the components of the $a^1\Delta_g$ state of $C_2H_2^{++}$ and half the difference between them ($\Delta V/2$) as a function of the *trans*-bending coordinate ρ_T (black and white circles, respectively). Solid line: the quadratic function obtained by fitting of the energy data in the range between $\rho_T = 0$ and 40°. Dash−dotted curve: quartic order function in ρ_T.

that all information needed can be extracted from a few potential energy values computed solely at planar nuclear arrangements. That was explicitly demonstrated in refs 18 and 19. Very reasonable agreement between the results of our previous ab initio studies and available experimental data has proven the reliability of other assumptions (e.g., neglect of the coupling between bending and stretching modes) involved in our model.

3. Method for Calculation of the Vibronic Structure in Δ Electronic States of Symmetric Four-Atomic Molecules

3.1. Potential Energy Curves for *trans* and *cis* Bending Vibrations. All the potential curves for the bending vibrations in the $a^1\Delta_g$ electronic state of $C_2H_2^{++}$ are computed at planar nuclear arrangements with the C−H and C−C bond lengths kept fixed at the values of 2.15 and 2.6 bohr, respectively. They are depicted in Figures 1−3. Instead of presenting the actually computed adiabatic potential curves for two electronic species correlating at the linear nuclear arrangement with the $a^1\Delta_g$ state, and split upon bending, we show the mean potential and half the difference between the adiabatic potentials

$$\bar{V} = \frac{V^+ + V^-}{2}, \frac{\Delta V}{2} = \frac{V^+ - V^-}{2} \qquad (1)$$

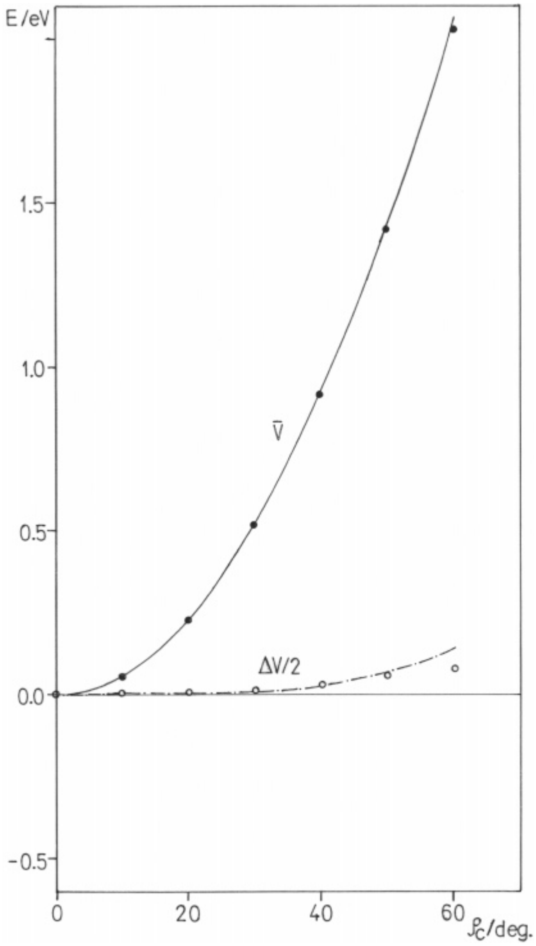

Figure 2. Ab initio computed values for the mean value ($\bar{V}$) of the adiabatic electronic energies and half the difference between them ($\Delta V/2$) as a function of the *cis*-bending coordinate ρ_C. For the key to notations, see Figure 1.

where V^+ and V^- represent respectively the states of A′ and A″ in the framework of the C_s point group. As seen from these figures, the molecule has linear equilibrium geometry in the electronic state in question.

At the *trans* bending, i.e., in the C_{2h} point group (Figure 1), the splitting of the potential curves is relatively large, with the B_g component of the Δ_g state (that correlates with an A'' species in the C_s subgroup of C_{2h}) lying above its A_g (A') counterpart. In the present study, we are only interested in low-lying vibronic levels of the $a^1\Delta_g$ electronic state and thus we focus our attention to the behavior of the potential energy surfaces in the region of the bending coordinates ρ_T, ρ_C (ρ_T is the supplement of the H−C−C bond angle at collective *trans* displacements of the hydrogen nuclei, and ρ_C is the analogous quantity for the *cis* bending) between 0 and 40 degrees. In this geometry range, the mean potential for the *trans* bending vibrations is reliably represented by a quadratic function in ρ_T (shown as a solid line in Figure 1), while the quantity $\Delta V/2$ is fitted as a function involving only the ρ_T^4 term, in accordance with the theory of the RT effect in Δ electronic states at small distortions of linearity.[5−8] Deviation of the ab initio computed energies at larger ρ_T values from these curves indicates that the model applied ceases to be reliable at strongly bent geometries. At the *cis* bending vibrations, i.e., within the C_{2v} point group (Figure 2), the splitting of the potential curves is extremely small, and, in this case, the A_1 (A' in the C_s point group) state lies slightly above the B_1 (A'') component. As in the case of the *trans* vibrations, in the range of ρ_C between 0 and 40 degrees,

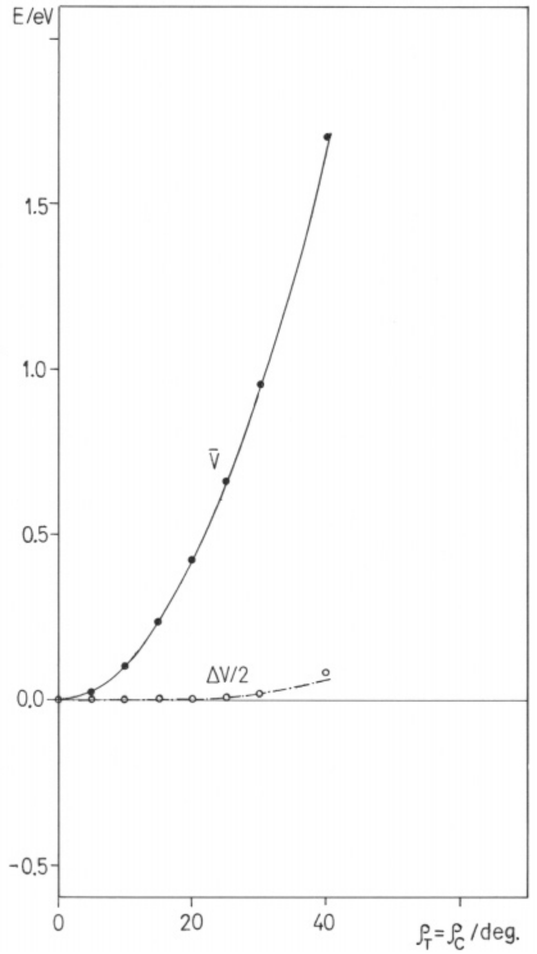

Figure 3. Ab initio computed values for the mean value ($\bar{V}$) of the adiabatic electronic energies and half the difference between them ($\Delta V/2$) as a function of one of the H−C−C bond angles at another H−C−C angle kept fixed at the zero value. For the key to notations, see Figure 1.

the mean potential and the difference between the component electronic states are reliably reproduced by the functions of second and quartic order, respectively, in the bending coordinate ρ_C. In Figure 3 are given the mean potential and the quantity $\Delta V/2$ computed at one of the H−C−C bending angles (say ρ_1) varied and the other H−C−C angle (ρ_2) kept fixed at the zero value. This coordinate ρ_1 is thus equal to the sum of $\rho_T/2$ and $\rho_C/2$ with $\rho_T = \rho_C$.

According to the predictions followed from the theory of the RT effect Δ electronic states of symmetric (ABBA-type) four-atomic molecules at small distortions of linearity[5−8] and their above-mentioned specific forms of the potential curves, we assume the following expressions for the mean potential and $\Delta V/2$:

$$\bar{V} = \frac{1}{2} k_T {\rho_T}^2 + \frac{1}{2} k_C {\rho_C}^2 \qquad (2)$$

and

$$\frac{\Delta V}{2} = [{c'_T}^2 {\rho_T}^8 + {c'_C}^2 {\rho_C}^8 + {c'_{TC}}^2 {\rho_T}^4 {\rho_C}^4 + 2c'_T c'_{TC} {\rho_T}^6 {\rho_C}^2 \cos 2(\phi_T - \phi_C) + 2c'_C c'_{TC} {\rho_T}^2 {\rho_C}^6 \cos 2(\phi_T - \phi_C) + 2c'_T c'_C {\rho_T}^4 {\rho_C}^4 \cos 4(\phi_T - \phi_C)]^{1/2} \qquad (3)$$

where ϕ_T and ϕ_C respectively represent the angles between the instantaneous molecular planes at collective *trans* and *cis* bending vibrations and a space-fixed plane with the common *z*-axis. Expression 3 reduces at planar molecular geometries, i.e., at $(\phi_T - \phi_C) = 0$ or π to

$$\frac{\Delta V}{2} = c'_T {\rho_T}^4 + c'_C {\rho_C}^4 + c'_{TC} {\rho_T}^2 {\rho_C}^2 \qquad (4)$$

By fitting all the electronic energy points in the above-mentioned restricted geometry ranges, we obtain the following coefficients appearing in Expressions 2−4:

$$k_T = 0.114 \text{ hartree/rad}^2,\ k_C = 0.1374 \text{ hartree/rad}^2$$
$$c'_T = -0.0284 \text{ hartree/rad}^4,$$
$$c'_C = 0.000412 \text{ hartree/rad}^4,\ c'_T = 0.0362 \text{ hartree/rad}^4 \qquad (5)$$

The reduced masses for the *trans* and *cis* bending infinitesimal vibrations in the $a^1\Delta_g$ electronic state of $C_2H_2^{++}$, corresponding to the bond lengths used in the calculation, are

$$\mu_T = \frac{2mMr^2R^2}{m(R+2r)^2 + MR^2} = 5.85444, \qquad \mu_C = \frac{2mMr^2}{m+M} = 8.59545 \qquad (6)$$

relative to the mass of the ^{12}C atom equal to 12.0. In expressions 6, *m* and *M* represent the masses of hydrogen (1.007825) and carbon (12.0), and *r* and *R* are the H−C and C−C bond lengths, respectively.

3.2. The Model for Handling RT Effect in $^1\Delta$ Electronic States of Symmetric Four-Atomic Molecules. In the vibronic treatment to follow, we use the simplest possible Hamiltonian that incorporates the terms contributing to the RT effect in Δ electronic states of tetra-atomic molecules. It can be written in the form

$$H = H_0 + H' \qquad (7)$$

with

$$H_0 = -\frac{1}{2\mu_T}\left(\frac{\partial^2}{\partial {\rho_T}^2} + \frac{1}{\rho_T}\frac{\partial}{\partial \rho_T} + \frac{1}{{\rho_T}^2}\frac{\partial^2}{\partial {\phi_T}^2}\right) - \frac{1}{2\mu_C}\left(\frac{\partial^2}{\partial {\rho_C}^2} + \frac{1}{\rho_C}\frac{\partial}{\partial \rho_C} + \frac{1}{{\rho_C}^2}\frac{\partial^2}{\partial {\phi_C}^2}\right) + \frac{1}{2} k_T {\rho_T}^2 + \frac{1}{2} k_C {\rho_C}^2 \qquad (8)$$

and

$$H' = c'_T {\rho_T}^4 [e^{4i(\theta - \phi_T)} + e^{-4i(\theta - \phi_T)}] + c'_C {\rho_C}^4 [e^{4i(\theta - \phi_C)} + e^{-4i(\theta - \phi_C)}] + c'_{TC} {\rho_T}^2 {\rho_C}^2 [e^{i(4\theta - 2\phi_T - 2\phi_C)} + e^{-i(4\theta - 2\phi_T - 2\phi_C)}] \qquad (9)$$

where θ is the coordinate conjugate to the component of the electronic angular momentum L_z along the *z*-axis that coincides at the linear nuclear arrangements with the molecular axis. Thus, we assume the stretching and end-over-end rotations to be separable from the degrees of freedom directly involved in the RT effect. For the sake of simplicity (and consistency) we use the kinetic energy operator corresponding to the infinitesimal bending vibrations. The quantum number *K* for the projection

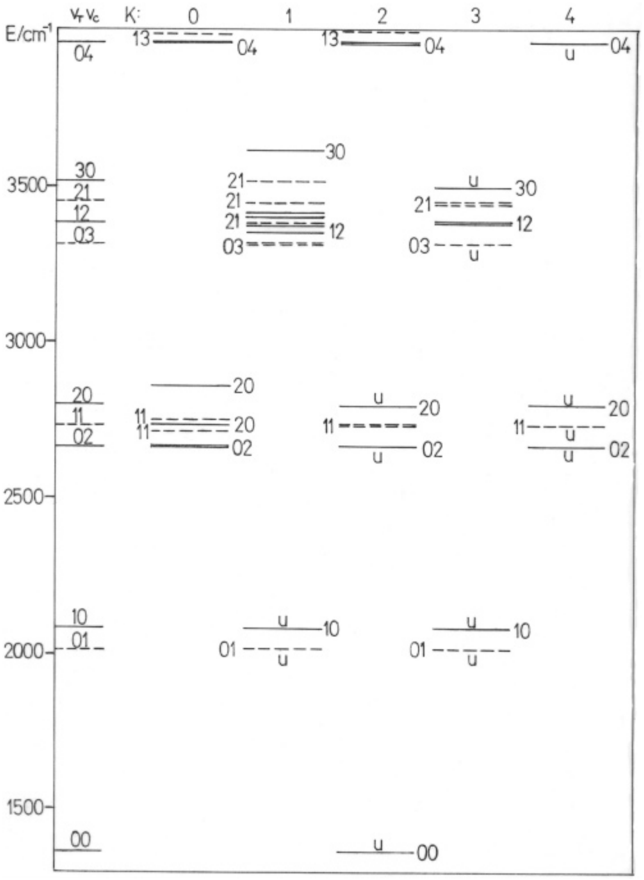

Figure 4. Graphical presentation of the low-lying part of the vibronic spectrum of the $a^1\Delta_g$ state of $C_2H_2^{++}$. Left-hand side (short lines): zero-order vibronic levels. Solid (longer) lines represent levels of *g* symmetry, and dashed lines represent those of *u* symmetry. Zero on the energy scale corresponds to the minimum of the potential surface for bending vibrations. Vibronic levels are labeled by the values of the quantum numbers υ_T and υ_C. *Unique*-type vibronic levels are denoted by *u* (Please note that, in this case, the symbol *u* does not denote the *u*-symmetry.).

of the total angular momentum on the *z*-axis is assumed to be a good quantum number. It is given by

$$K = |l_T + l_C \pm \Lambda| \tag{10}$$

where l_T and l_C are the quantum numbers for the vibrational angular momenta at the *trans* and *cis* bending vibrations, respectively, and Λ (= 2) is the quantum number corresponding to L_z. For technical reasons, it is convenient to introduce the dimensionless bending coordinates q_T and q_C by the relations

$$q_\alpha = \sqrt{\lambda_\alpha}\rho_\alpha,\ \lambda_\alpha = \sqrt{k_\alpha \mu_\alpha} = \mu_\alpha \omega_\alpha,\ \alpha = \mathrm{T,C} \tag{11}$$

We employ as a basis functions in the variational handling, as well as zero-order vibronic functions in the perturbative treatment of the problem in question

$$|\upsilon_T, l_T, \upsilon_C, l_C, +\rangle \equiv (2\pi)^{-3/2}\, \xi(\rho_e, z_e) e^{2i\theta}\, e^{il_T\phi_T}\, e^{il_C\phi_C}\, R_{\upsilon_T l_T}(q_T) R_{\upsilon_C l_C}(q_C)$$

$$|\upsilon'_T, l'_T, \upsilon'_C, l'_C, - \equiv (2\pi)^{-3/2}\, \xi(\rho_e, z_e) e^{-2i\theta}\, e^{il'_T\phi_T}\, e^{il'_C\phi_C}\, R_{\upsilon'_T l'_T}(q_T) R_{\upsilon'_C l'_C}(q_C) \tag{12}$$

where $\xi(\rho_e,z_e)$ is the part of the electronic wave functions that depends on all the electronic coordinates except those of θ, and

$$R_{\upsilon_\alpha l_\alpha}(q_\alpha) = N_{\upsilon_\alpha l_\alpha} L_{\upsilon_\alpha l_\alpha}(q_\alpha) e^{-1/2 q_\alpha^{\,2}} \tag{13}$$

are the eigenfunctions of the "radial" equation for an isotropic two-dimensional harmonic oscillator. υ_α is the bending quantum number; for a given υ_α, the possible values of l_α are υ_α, $\upsilon_\alpha - 2$, ..., $-\upsilon_\alpha$. After integrating over the electronic coordinates, the parts of the model Hamiltonian (eqs 8 and 9) take the forms

$$H_0 = \left\{ -\frac{1}{2}\left(\frac{\partial^2}{\partial {q_T}^2} + \frac{1}{q_T}\frac{\partial}{\partial q_T} - \frac{{l_T}^2}{{\rho_T}^2} \right) + \frac{1}{2}{q_T}^2 \right\}\omega_T + \left\{ -\frac{1}{2}\left(\frac{\partial^2}{\partial {q_C}^2} + \frac{1}{q_C}\frac{\partial}{\partial q_C} - \frac{{l_C}^2}{{\rho_C}^2} \right) + \frac{1}{2}{q_C}^2 \right\}\omega_C \tag{14}$$

and

$$H' = c_T \omega_T {q_T}^4 [e^{-4i\phi_T} + e^{4i\phi_T}] + c_C \omega_C {q_C}^4 [e^{-4i\phi_C} + e^{4i\phi_C}] + c_{TC}\sqrt{\omega_T \omega_C}\, {q_T}^2 {q_C}^2 [e^{-2i(\phi_T + \phi_C)} + e^{2i(\phi_T + 2\phi_C)}] \tag{15}$$

with the values

$$\omega_T = 717.33 cm^{-1},\ \omega_C = 649.94 cm^{-1},\ c_T = -0.007145,\ c_C = 0.00006463,\ c_{TC} = 0.007192 \tag{16}$$

TABLE 1: Low-Lying Part of the Vibronic Spectrum in the $a^1\Delta_g$ State of $C_2H_2^{++}$ [a]

υ_T	υ_C	K	$E^{(0)}$	$E^{(1)}$	$E^{(2)}$	E_p	E_v
0	0	2	1367.27	0.00	−0.25	1367.01	1367.01
0	1	3	2017.21	0.00	−0.33	2016.88	2016.88
0	1	1	2017.21	0.00	−0.39	2016.81	2016.81
1	0	3	2084.60	0.00	−1.20	2083.40	2083.39
1	0	1	2084.60	0.00	−2.16	2082.44	2082.41
0	2	4	2667.14	0.00	−0.43	2666.71	2666.71
0	2	2	2667.14	0.00	−0.59	2666.55	2666.54
0	2	0	2667.14	−0.50	−1.24	2665.40	2665.62
0	2	0	2667.14	0.50	−1.24	2665.41	2665.73
1	1	4	2734.54	0.00	−1.42	2733.12	2733.11
1	1	2	2734.54	0.00	−3.02	2731.52	2731.48
1	1	2	2734.54	0.00	−1.11	2733.43	2733.41
1	1	0	2734.54	−19.64	−2.29	2712.61	2712.49
1	1	0	2734.54	19.64	−2.29	2751.88	2751.93
2	0	4	2801.94	0.00	−3.51	2798.43	2798.37
2	0	2	2801.94	0.00	−8.53	2793.41	2793.22
2	0	0	2801.94	−61.48	−3.35	2737.11	2737.16
2	0	0	2801.94	61.48	−3.35	2860.07	2860.28
0	3	5	3317.08	0.00	−0.57	3316.50	3316.50
0	3	3	3317.08	0.00	−0.84	3316.24	3316.23
0	3	1	3317.08	−0.87	−2.19	3314.01	3313.60
0	3	1	3317.08	0.87	−2.19	3315.76	3315.19
1	2	5	3384.47	0.00	−1.73	3382.74	3382.71
1	2	3	3384.47	0.00	−3.89	3380.58	3380.51
1	2	3	3384.47	0.00	−1.41	3383.06	3383.06
1	2	1	3384.47				3353.27
1	2	1	3384.47				3376.46
1	2	1	3384.47				3413.21
2	1	5	3451.87	0.00	−3.93	3447.94	3447.87
2	1	3	3451.87	0.00	−10.27	3441.60	3441.36
2	1	3	3451.87	0.00	−3.37	3448.50	3448.44
2	1	1	3451.87				3381.03
2	1	1	3451.87				3444.75
2	1	1	3451.87				3515.50
3	0	5	3519.27	0.00	−8.04	3511.23	3510.98
3	0	3	3519.27	0.00	−21.51	3497.76	3497.04
3	0	1	3519.27	−106.49	−8.60	3404.18	3403.22
3	0	1	3519.27	106.49	−8.60	3617.16	3617.73

[a] $E^{(0)}$, $E^{(1)}$, $E^{(2)}$, and E_p represent the zero-order energy, the first- and second-order corrections, and the complete second-order perturbative energy, respectively. E_v values are the results of variational computations.

TABLE 2: Low-Lying $K = 0-3$ Vibronic Energy Levels (in cm^{-1}) of the $a^1\Delta_g$ State of $C_2H_2^{++}$ and $C_2D_2^{++}$, Relative to the Lowest-Lying ($K = 2$) Vibronic Level[a]

	$C_2H_2^{++}$		$C_2D_2^{++}$	
	g	*u*	*g*	*u*
$K = 0$	1299	1345	954	1058
	1299	1385	954	1082
	1370	2623	1144	2000
	1493	2644	1229	2023
	2595	2654	1907	2023
	2596	2680	1909	2048
$K = 1$	715	650	593	477
	1986	1947	1530	1431
	2009	1948	1547	1432
	2036	2014	1564	1617
	2046	2078	1704	1661
	2251	2148	1851	1709
$K = 2$	0	1364	0	1070
	1300	1366	954	1071
	1426	2628	1184	2003
	2594	2657	1907	2024
	2598	2681	1909	2045
	2658	2701	2091	2177
$K = 3$	716	650	594	477
	2014	1949	1547	1431
	2016	2074	1548	1660
	2130	2081	1770	1664
	3271	3240	2477	2384
	3304	3247	2501	2386

[a] *g* and *u* denote "gerade" and "ungerade" vibronic levels, respectively.

We know, of course, that the present theoretical treatment does not guarantee such an accuracy, which would justify giving the bending frequencies with so many significant digits; however, we write these numbers in such a form, because we will discuss below the (extremely small) discrepancies between the variational and truncated perturbative handling of the problem. The numbers given in eq 16 are consistent with the ab initio results of Furuhashi et al.[11] who obtained 950 and 461 cm^{-1} for *trans*, and 667 and 627 cm^{-1} for *cis* bending vibrational frequencies, concerning both the magnitude of the mean frequencies for two adiabatic components of the $a^1\Delta_g$ state, the moderate splitting of the potential curves in the former, and very small splitting in the latter case. However, a precise comparison of the corresponding numbers is not possible, because of the special kind of the fitting procedure employed in the present study. We have namely the following situation: In the case of Π electronic states, when handled in the lowest-order (quadratic) approximation, the bending frequencies for the upper and lower (adiabatic) potential curve, split upon bending, ω_i^+ and ω_i^- (i = T, C), respectively, are connected with the mean frequency ω_i by the relation $\omega_i^{\pm} = \omega_i\sqrt{1\pm\epsilon_i}$, where ϵ_i is the quadratic "Renner parameter". In the present case (Δ electronic states), however, there is no splitting in the second-order of the coordinates ρ_i, and, consequently, the adiabatic potential energy curves remain degenerate in the harmonic approximation. On the other hand, if the splitting (of the fourth-order in ρ_i) is taken into account, the adiabatic potential energy curves cannot be fitted reliably by quadratic functions, and thus the above simple formula cannot be applied for determining $\omega_i^{\pm}$.

3.3. Perturbative Approach. Second-order perturbative formulas for vibronic levels in Δ electronic states of symmetric four-atomic molecules with the linear equilibrium geometry have already been published in refs 6 and 7. However, they concern somewhat more complicated cases than the present one [multiplet electronic states, the presence of quatric terms connecting the basis functions with the same Δ (i.e., +2 or −2) value], and thus they differ in some cases from those we give below for the simplest possible model for Δ states (i.e., they cannot be simply reduced to the latter ones), represented by Hamiltonians 14 and 15. As stated many times, in the case of four-atomic molecules it is not possible to derive the perturbative formulas for all possible combinations of the vibronic quantum numbers, because the zero-order energy levels become continuously more degenerate with increasing values of υ_T and υ_C. Fortunately, they can be simply obtained for the majority of the low-lying vibronic levels, which are of most importance, because they are usually observed in experiments, and, on the other hand, the reliability of the model employed is less reliable for higher-energy levels. We consider the following cases:

(a) $\upsilon_C = 0$ (The formulas for the opposite case, namely, $\upsilon_T = 0$, are simply obtained by interchanging the indices T and C in the formulas given below.)

The zero-order energy is given by

$$E^{(0)} = (\upsilon_T + 1)\omega_T + \omega_C \tag{17}$$

There are three particular cases: (a1) $K = \upsilon_T + 2 (= K_{\max})$ The zero-order vibronic wave function is $|\upsilon_T, \upsilon_T, 0,0, +\rangle$. The first-order energy correction is $E^{(1)} = 0$. The second-order energy correction is given by

$$E^{(2)} = -\frac{1}{4}(\upsilon_T + 1)(\upsilon_T + 2)(\upsilon_T + 3)(\upsilon_T + 4){c_T}^2\omega_T - 6{c_C}^2\omega_C - (\upsilon_T + 1)(\upsilon_T + 2){c_{TC}}^2\frac{\omega_T\omega_C}{\omega_T + \omega_C} \tag{18}$$

(a.2) $K = \upsilon_T (= K_{\max} - 2)$ The zero-order vibronic wave function is $|\upsilon_T, \upsilon_T - 2,0,0, +\rangle$. The first-order energy correction vanishes. The second-order energy correction is

$$E^{(2)} = -\frac{1}{4}\upsilon_T(\upsilon_T + 1)(\upsilon_T + 2)(\upsilon_T + 35){c_T}^2\omega_T - 6{c_C}^2\omega_C - \upsilon_T{c_{TC}}^2\omega_T\left[4 + (\upsilon_T + 1) + \frac{\omega_C}{\omega_T + \omega_C}\right] \tag{19}$$

Both cases a.1 and a.2 represent so-called *unique* vibronic states.[20] (a.3) $K < \upsilon_T$ The zero-order energy level is two-fold degenerate. The corresponding vibronic functions are $|\upsilon_T, K + 2,0,0, -\rangle$ and $|\upsilon_T, K - 2,0,0, +\rangle$. The first-order energy correction is

$$E^{(1)}_{1/2} = \mp\frac{3}{2}c_T\omega_T\sqrt{({\upsilon_T}^2 - K^2)[(\upsilon_T + 2)^2 - K^2]} \tag{20}$$

and the second-order correction is given by

$$E^{(2)}_{1/2} = -\frac{1}{4}(\upsilon_T + 1)[17\upsilon_T(\upsilon_T + 2) + 4K^2]{c_T}^2\omega_T - 6{c_C}^2\omega_C - \frac{1}{2}{c_{TC}}^2\omega_T\left[2({\upsilon_T}^2 - K^2 + 2\upsilon_T) + ({\upsilon_T}^2 + K^2 + 2\upsilon_T)\frac{{\omega_C}^2}{{\omega_C}^2 - {\omega_T}^2}\right] \tag{21}$$

(b) $K = \upsilon_T + \upsilon_C + 2 (= K_{\max})$ This is an *unique* level corresponding to the zero-order vibronic wave function $|\upsilon_T, \upsilon_T, \upsilon_C, \upsilon_C, +\rangle$. The zero-order energy is

$$E^{(0)} = (\upsilon_T + 1)\omega_T + (\upsilon_C + 1)\omega_C \tag{22}$$

The first-order perturbative correction vanishes. The second-order correction is

$$E^{(2)} = -\frac{1}{4}(v_{\rm T}+1)(v_{\rm T}+2)(v_{\rm T}+3)(v_{\rm T}+4)c_{\rm T}^{\,2}\omega_{\rm T} - \frac{1}{4}(v_{\rm C}+1)(v_{\rm C}+2)(v_{\rm C}+3)(v_{\rm C}+4)c_{\rm C}^{\,2}\omega_{\rm C} - \frac{1}{2}(v_{\rm T}+1)(v_{\rm T}+2)(v_{\rm C}+1)(v_{\rm C}+2)c_{\rm TC}^{\,2}\frac{\omega_{\rm T}\omega_{\rm C}}{\omega_{\rm T}+\omega_{\rm C}} \quad (23)$$

For $v_{\rm C} = 0$, formulas 22 and 23 reduce to 17 and 18, respectively.

(c) $K = v_{\rm T} + v_{\rm C}$ $(= K_{\max} - 2)$

There are two zero-order vibronic functions corresponding to this case, $|v_{\rm T}, v_{\rm T}, v_{\rm C}, v_{\rm C} - 2, +\rangle$ and $|v_{\rm T}, v_{\rm T} - 2, v_{\rm C}, v_{\rm C}, +\rangle$. The zero-order energy is given by eq 22. The degeneracy of the corresponding vibronic level is not resolved in the first-order perturbation theory, and this represents the difference compared to the case when a more general Hamiltonian is used, like in refs 6 and 7. The second-order correction is given by

$$E^{(2)}_{1/2} = \frac{1}{2}(H_{11} + H_{22}) \mp \frac{1}{2}\sqrt{(H_{11} - H_{22})^2 + 4H_{12}^{\,2}} \quad (24)$$

where

$$H_{11} = -\frac{1}{4}(v_{\rm T}+1)(v_{\rm T}+2)(v_{\rm T}+3)(v_{\rm T}+4)c_{\rm T}^{\,2}\omega_{\rm T} - \frac{1}{4}v_{\rm C}(v_{\rm C}+1)(v_{\rm C}+2)(v_{\rm C}+35)c_{\rm C}^{\,2}\omega_{\rm C} - \frac{1}{2}v_{\rm C}(v_{\rm T}+1)(v_{\rm T}+2)c_{\rm TC}^{\,2}\omega_{\rm C}\left[4 + (v_{\rm C}+1)\frac{\omega_{\rm T}}{\omega_{\rm T}+\omega_{\rm C}}\right] \quad (25)$$

$$H_{12} = -4\sqrt{v_{\rm T}v_{\rm C}}\,c_{\rm TC}\sqrt{\omega_{\rm T}\omega_{\rm C}}\,[(v_{\rm T}+1)(v_{\rm T}+2)c_{\rm T} + (v_{\rm C}+1)(v_{\rm C}+2)c_{\rm C}] \quad (26)$$

and the term H_{22} is obtained from eq 25 by interchanging the indices T and C.

(d) $v_{\rm T} = 1$, $v_{\rm C} = 1$, $K = 0$

In the general case, the zero-order vibronic levels are more than two-fold degenerate, and the perturbative handling is more complicated. An important exception is when $v_{\rm T} = 1$, $v_{\rm C} = 1$, $K = 0$. There are two corresponding vibronic wave functions: $|1,1,1,1,-\rangle$ and $|1,-1,1,-1,+\rangle$. The zero-order energy and the first- and second-order corrections are then

$$E^{(0)} = 2\omega_{\rm T} + 2\omega_{\rm C} \quad (27)$$

$$E^{(1)}_{1/2} = \mp 4c_{\rm TC}\sqrt{\omega_{\rm T}\omega_{\rm C}} \quad (28)$$

and

$$E^{(2)}_{1/2} = -54c_{\rm T}^{\,2}\omega_{\rm T} - 54c_{\rm C}^{\,2}\omega_{\rm C} - 2c_{\rm TC}^{\,2}\left(2\omega_{\rm T} + 2\omega_{\rm C} + \frac{\omega_{\rm T}\omega_{\rm C}}{\omega_{\rm T}+\omega_{\rm C}}\right) \quad (29)$$

3.4. Variational Approach. The variational computations are carried out for each K value separately; furthermore, the use is made from the fact that the vibronic basis functions corresponding to even values of $v_{\rm C}$ are of g, and those with odd $v_{\rm C}$ of u symmetry, enabling further block-diagonalization of the Hamiltonian matrix. Moreover, the $K = 0$ (Σ) blocks can be divided into + and − subblocks. The basis sets employed in the present study involve the bending functions up to $v_{\rm T} = v_{\rm C} = 9$ with all compatible $l_{\rm T}$ and $l_{\rm C}$. The dimensions of the corresponding secular equations do not exceed about 200. The basis sets of such dimensions ensure full convergence (up to 0.01 cm^{-1}) for all the vibronic levels presented.

4. Results and Discussion

The low-lying vibronic energy levels of the $a^1\Delta_g$ state of $C_2H_2^{++}$ computed in the framework of the present study are given in Tables 1 and 2 and Figure 4. Table 1 contains the results obtained by using the perturbative formulas from Section 3.3 and the variational approach briefly described in Section 3.4. First let us note that the perturbative formulas presented in Section 3.3 cover almost all the cases corresponding to the combinations of $v_{\rm T}$ and $v_{\rm C}$ with their sum not exceeding 3. An inspection of the content of Table 1 shows that the discrepancy between the energies computed in the second-order perturbation theory (E_p) and their variationally calculated counterparts, E_v, (which correspond to a complete perturbative treatment) are in no case larger than 1 cm^{-1} and, in the great majority of cases, much smaller. This is of no special practical interest in the present case, but clearly shows that the perturbative formulas can be reliably used when there is no program package available for a variational handling of the same problem, as in the case of more than four-atomic molecules.[21,22] A difference between the RT effect in Δ electronic states of polyatomic (in the present case, four-atomic) molecules and that for the classical example of triatomics is the appearance of more than two *unique* levels for each quantum number K in the former case. Such are, for example, in the case of $K = 4$, the levels corresponding to the zero-order species $|0,0,2,2,+\rangle$, $|1,1,1,1,+\rangle$, $|2,2,0,0,+\rangle$, $|0,0,4,2,+\rangle$, $|4,2,0,0,+\rangle$.

Table 2 lists also the variationally computed vibronic energies of the $C_2D_2^{++}(a^1\Delta_g)$ isotopomer. The harmonic *trans* and *cis* bending frequencies corresponding to the mean *trans* and *cis* bending potentials curves are, in the case of $C_2D_2^{++}$, 549.17 and 477.21 cm^{-1}, respectively. Thus, the computed ratios of the *trans* and *cis* bending frequencies in $C_2H_2^{++}$ and $C_2D_2^{++}$ are 1.207 and 1.362. However, the numbers given in Table 2 cannot be directly used for predicting the isotopic shifts in the bending spectra of $C_2H_2^{++}$ and $C_2D_2^{++}$ because they are given with respect to the lowest-lying bending levels of these isotopomers, i.e., they do not take into account the different zero-point energies involving all vibrational modes of these species.

5. Conclusions

In this study we present the results of ab initio calculation of the low-lying part of the vibronic spectrum in the $a^1\Delta_g$ state of $C_2H_2^{++}$ and $C_2D_2^{++}$ obtained by employing a perturbative and a variational approach. It is shown that, in the concrete case, they give almost identical results, what means that a perturbative treatment of the RT effect in polyatomic molecules with linear equilibrium geometry can reliably be used instead of a corresponding variational procedure. The computations presented in this study are carried out in the framework of a very simple model. Consequently, they cannot compete in accuracy with those achieved by employing highly sophisticated approaches that can be applied in the case of much simpler triatomic species (as, e.g., in the benchmark study on the X^2B_1, $A^2A_1 - {}^2\Pi$ system of NH_2[23]). It is to be expected that the numerical inaccuracy of the results shown in Table 1 and Figure 4 continuously grows with increasing energy, reaching magnitude on the order of 100

cm^{-1} for the highest levels presented. However, the present pragmatic approach gains attractiveness in handling larger dicationic systems, for which the more accurate treatments would be hardly feasible.

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References and Notes

(1) Thissen, R.; Delwiche, J.; Robbe, J. M.; Duflot, D.; Flament, J.-P.; Eland, J. H. D. *J. Chem. Phys.* **1993**, *99*, 6590 and references therein.

(2) Duflot, D. J.; Robbe, M.; Flament, J.-P. *J. Chem. Phys.* **1995**, *102*, 355.

(3) Kinugawa, T.; Lablanquie, P.; Penent, F.; Palaudoux, J.; Eland, J. H. D. *J. Electron Spectrosc. Relat. Phenom.* **2004**, *141*, 143 and reference therein.

(4) Zyubina, T. S.; Dyakov, Y. A.; Lin, S. H.; Bandrauk, A. D.; Mebel, A. M. *J. Chem. Phys.* **2005**, *123*, 134320 and references therein.

(5) Perić, M.; Marian, C. M.; Engels, B. *Mol. Phys.* **1999**, *97*, 731.

(6) Perić, M.; Ostojić, B. *Mol. Phys.* **1999,** *97*, 743.

(7) Perić, M.; Peyerimhoff, S. D. *J. Mol. Spectrosc.* **2002**, *212*, 153.

(8) Perić, M.; Jerosimić, S.; Ranković, R.; Krmar, M.; Radić-Perić, J. *J. Chem. Phys.* **2006,** *330*, 60.

(9) Ohrendorf, E. M.-L.; Tarantelli, F.; Cederbaum, S. *J. Chem. Phys.* **1990**, *92*, 2984.

(10) Andrews, S. R.; Harris, F. M.; Parry, D. E. *Chem. Phys.* **1992**, *166*, 69.

(11) Furuhashi, O.; Kinugawa, T.; Masuda, S.; Yamada, C.; Ohtani, S. *Chem. Phys. Lett.* **2001**, *342*, 626.

(12) Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1985**, *115*, 259.

(13) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys*. **1988**, *89*, 5803.

(14) Knowles, J.; Werner, H.-J. *Chem. Phys. Lett.* **1988**, *145*, 514.

(15) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(16) MOLPRO is a ab initio package written by H. J. Werner and P. J. Knowles. Further details can be found at http://www.molpro.net.

(17) Perić, M.; Ostojic, B.; Radić-Perić, J. *Phys. Rep.* **1997**, *290*, 283.

(18) Peric, M.; Peyerimhoff, S. D. In *The Role of Degenerate States in Chemistry*; Baer, M., Billing, G. D., Eds.; Advances in Chemical Physics Series; Wiley & Sons, Inc.: New York, 2002; Vol. 124, p 583.

(19) Perić, M. C.; Marian, M.; Peyerimhoff, S. D. *J. Chem. Phys.* **1999**, *114*, 6086.

(20) Jungen, Ch.; Merer, A. J. In *Molecular Spectroscopy: Modern Research*; Rao, K. N., Ed.; Academic Press: San Diego, CA, 1977; Vol. 2, p 127.

(21) Perić, M. *Mol. Phys.* **2007**, *105*, 59.

(22) Perić, M.; Petković, M.; Jerosimić, S. *Chem. Phys.*, in press.

(23) Gabriel, W.; Chambaud, G.; Rosmus, P.; Carter, S.; Handy, N. C. *Mol. Phys.* **1994**, *81*, 1445.