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***Ab initio* study of the ground and excited electronic states of the methyl radical**

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Abstract

The ground and some excited electronic states of the methyl radical have been characterized by means of highly correlated *ab initio* techniques. The specific excited states investigated are those involved in the dissociation of the radical, namely the $3s$ and $3p_z$ Rydberg states, and the A_1 and B_1 valence states crossing them, respectively. The C-H dissociative coordinate and the HCH bending angle were considered in order to generate the first two-dimensional *ab initio* representation of the potential surfaces of the above electronic states of CH_3 , along with the nonadiabatic couplings between them. Spectroscopic constants and frequencies calculated for the ground and bound excited states agree well with most of the available experimental data. Implications of the shape of the excited potential surfaces and couplings for the dissociation pathways of CH_3 are discussed in the light of recent experimental results for dissociation from low-lying vibrational states of CH_3 . Based on the *ab initio* data some predictions are made regarding methyl photodissociation from higher initial vibrational states.

1 Introduction

Methyl radical is a metastable colourless gas, which is a precursor to other hydrocarbons in the petroleum cracking industry. It has been called the 'free radical' because of its extremely reactive nature. CH_3 lifetime is only a few millionths of a second, making arduous the laboratory studies and converting into essential tools the state-of-the art theoretical procedures to acquire information and to predict properties about the isolated species and its reactivity. However, although the molecular size is optimal to use accurate levels of theory to compute excitations to the excited electronic states describing cross intersections and non-adiabatic couplings, few theoretical works have currently reported a detailed structural and spectroscopic characterization.

The CH_3 radical is viewed as the species responsible for relevant astrochemical processes. In particular, it is assumed to be a key species to the formation of complex hydrocarbon

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molecules. Its presence in astrophysical sources was first predicted by Herzberg et al. [1–2], and is commonly included in astrochemical models. In 1973, Herbst and Klemperer [3] considered it in the basic ion-molecule gas-phase chemistry networks in the interstellar medium driven by cosmic-ray ionization. In 2000, Feuchtgruber et al. [4] detected it with the Infrared Space Observatory through the out-of-plane bending mode ν_2 . A Q -branch at 16.5 mm and the $R(0)$ line at 16.0 mm were unambiguously observed toward the Galactic center Sagittarius A [4].

Herzberg and Shoosmith [1] and Herzberg [2] first assumed a D_{3h} symmetry for CH_3 . The planar structure along with the extreme reactivity delayed its astrophysical discovery and made the radical undetectable for many spectroscopic techniques. Methyl does not possess a permanent electric dipole moment, which is crucial for rotational spectroscopy. The ground electronic state rovibrational structure has been explored with vibrational and rovibrational spectroscopy techniques in gas phase and solid matrices [5–22] although, with the exception of the ν_2 out-of-plane bending mode, infrared active transitions are very weak [7, 11]. Different gas phase Raman techniques and high-resolution infrared techniques have been applied to the analysis of the ν_1 symmetric stretching [5–9] and the degenerate ν_3 asymmetric stretch mode [14–20], respectively. The ν_2 mode, key for the astrophysical detection, has been studied in gas phase by Tan et al. [10], Yamada et al. [11], Wormhoudt et al. [12], and Amano et al. [13].

The planar symmetry implies that many one-photon transitions to the excited states of CH_3 are forbidden. Electronic transitions involving valence and Rydberg states have been reported to understand the photodissociation dynamics and to facilitate the astronomical detection [1,2,23–34]. Herzberg and Shoosmith [1] published in 1956 the first ultraviolet absorption spectrum and assigned the band observed at 216 nm to the origin of the excitation spectrum corresponding to the $3s$ Rydberg state. It corresponds to the excitation of the unpaired electron of an orbital with carbon $2p_z$ character into the $3s$ carbon-based orbital. Further studies like those of Callear and Metcalfe [24] and Westre et al. [29] examined the structure and dynamics of the vibronic levels above the origin by far-ultraviolet resonance Raman spectroscopy. Recently, Settersten et al. [31] used coherent double-resonance techniques.

The photodissociation dynamics of methyl from the $3s$ Rydberg state was firstly studied by Wilson et al. [35] using the H-atom Rydberg tagging technique. They assigned the narrow peak observed in the measured internal energy distribution of the CH_2 fragment to the $\text{CH}_2(1^1A_1) + \text{H}(^2S)$ channel. The later observations of North *et al.* [36] using photofragment translational spectroscopy were consistent with the perpendicular one-photon transition $\tilde{B}^2A_1 \leftarrow \tilde{X}^2A_2''$ to the $3s$ Rydberg state. More recently, Wu *et al.* [37] employed the H-atom Rydberg tagging time-of-flight technique. The development of multiphoton spectroscopy techniques, especially resonance enhanced multiphoton ionization (REMPI), enabled the acquisition of new information on excited states [26]. In particular, two-photon transitions to the $3p_z$ and $4p_z$ Rydberg states were identified and have become widely used for detection of methyl radicals in the gas phase [27,34].

In a previous paper [38], we studied the predissociation dynamics of selected, low-lying vibrational states of the $3p_z$ Rydberg state of CH_3 and CD_3 using a novel methodology based on a femtosecond three-color experiment to generate two-photon excitation and ionize methyl radicals as a function of time, in combination with velocity map imaging detection. In a second paper [39] we completed the study of the photodissociation dynamics of the methyl radical from the $3s$ and $3p_z$ Rydberg states using the velocity map and slice ion imaging in combination with pump-probe nanosecond laser pulses. The methyl radicals were excited through 0^0_0 transitions either to the $3s$ Rydberg state at 216 nm through a one-photon process, or to the $3p_z$ Rydberg state at 333.45 nm in a two-photon process. The produced $\text{H}(^2S)$ photofragments were detected using a (2+1) REMPI scheme at 243.2 nm. The work highlights different dissociation mechanisms for the $3s$ and $3p_z$ Rydberg states.

In our earlier works [38,39], one-dimensional potential energy curves in the C-H dissociation coordinate were calculated and reported for the ground and the excited states involved in the dissociation processes of CH_3 , along with the relevant nonadiabatic couplings and conical intersections between those states. To this purpose, highly correlated *ab initio* methods were used. The experimental results were successfully interpreted with the aid of these new *ab initio* data. Previous theoretical studies on the electronic excited states were scarce [29,40–45]. In particular, Yu et al. [43] performed calculations using moderate levels of theory in order to obtain excitation energies for excited states and to discuss the possible fragmentation pathways, $\text{CH}_3 \rightarrow \text{CH}_2 + \text{H}$ and $\text{CH}_3 \rightarrow \text{CH} + \text{H}_2$, for the $3s$ and $3p$ Rydberg states, but couplings between states were not considered.

While the one-dimensional *ab initio* picture recently reported has proven very useful in the interpretation of the experimental data [38,39], a more precise theoretical characterization of such an important radical species like CH_3 would be highly desirable. This can be achieved by considering the HCH bending mode in the *ab initio* computations, in addition to the C-H dissociation coordinate. This is the goal of the present work, which reports two-dimensional (2D) potential-energy surfaces of the ground and excited electronic states relevant for the CH_3 dissociation processes and the electronic couplings between them, for the first time. The excited states investigated are the $3s$ and $3p_z$ Rydberg states, and the two valence dissociative states crossing them. The implications of the angular dependence of the potential surfaces and couplings for the different dissociation processes of CH_3 are discussed in detail.

The paper is organized as follows. In Section 2 the methodology used and the computational details are described. Results are presented and discussed in Section 3. Finally, some conclusions are given in Section 4.

2 Theoretical Methodology

2.1 Electronic structure calculations

The electronic structure calculations were performed using the MOLPRO [46] and GAUSSIAN packages [47] and state of the art *ab initio* procedures. Explicitly correlated coupled cluster methods (RCCSD(T)-F12) [48], state-average complete active space self-consistent field (SA-CASSCF) [49] and internally contracted multi reference configuration

interaction (MRCI) [50] methods were employed to characterize the ground and the first seven excited electronic states of methyl radical with A_1 and B_1 symmetries. Moller-Plesset theory was employed to determine the anharmonic force field. The aug-cc-pVTZ augmented correlation consistent basis set of Dunning [51], denoted in this paper by AVTZ, was used in all of the calculations.

The favored geometry and the harmonic frequencies corresponding to the $\tilde{X}^2A_2''$ ground electronic state were obtained with RCCSD(T)-F12, using the MOLPRO default options. The atomic orbitals were described by the AVTZ basis set in connection with the corresponding basis sets for the density fitting and the resolutions of the identity (this ensemble is denoted by AVTZ-F12).

The excited electronic states were calculated at the MRCI/CASSCF level of theory. To describe their evolution during the radical dissociation process, two-dimensional potential energy surfaces depending on the two coordinates of Fig. 1, the R reaction coordinate and the α bending angle of the CH_2 group, were computed using a set of 680 geometries of C_{2v} symmetry. They were defined for 40 different values of R ranging from 0.6 Å to 20 Å, and 17 values of α ranging from 70° to 280°. The system was oriented with the dissociation coordinate along the z -axis so that C_{2v} states of CH_3 correlate to the states of the CH_2 fragments. The active space was defined using eleven orbitals, six of a_1 symmetry, three of b_1 symmetry, and two of b_2 symmetry. During the SA-CASSCF iterations, two inner orbitals were optimized and kept doubly occupied in all the configurations. For the MRCI treatment, the core orbital of the carbon atom was kept frozen. An active space of eleven orbitals was also selected for the determination of MRCI harmonic frequencies without symmetry.

2.2 Diabatization procedure and fitting

In principle, *ab initio* calculations provide electronic states in the adiabatic representation. However, the methyl radical exhibits excited electronic states, which are entangled due to nonadiabatic couplings between them. Adiabatic representations are therefore unrealistic and surface fittings are unfeasible. Indeed, obtaining a smooth fit of a multi-dimensional surface with plenty of irregularities due to avoided crossing effects is a complex task. Additionally, the sharp shape of the non-adiabatic coupling matrix elements (NACME) presents several drawbacks, as they require a large density of points to be properly characterized and they are impractical to fit.

Thus, the first step of our fitting approach consists of obtaining the different electronic states in a diabatic representation by using a new diabaticization procedure which does not require prior calculation of the NACMEs. Since couplings typically present a sharp radial dependence but a much smoother dependence on the HCH angle, the strategy adopted was to diabaticize the *ab initio* energies along the R dissociation coordinate independently for each value of α and for each symmetry group. For a given bending angle, the four adiabatic electronic states sharing symmetry a_i ($i=1-4$) are diabaticized along R to obtain diabatic states d_i ($i=1-4$) following a sequential 2x2 diabaticization scheme designed to construct the diabatic states d_i and d_j from their adiabatic representation a_i and a_j . Our scheme is based on the following assumptions:

- 1) Diabatic states cross only once (valid in our case).
- 2) The sum of the total energies of the electronic states is conserved,

$$\sum_{i=1}^N E_{a_i} = \sum_{i=1}^N E_{d_i} \quad [1]$$

where N is the number of electronic states with the same symmetry.

- 3) Outside the interaction region I (defined along the dissociation coordinate), diabatic potential energy curves match the adiabatic ones. The I region obeys the formula:

$$\Delta E < \Delta E_{\min} + \xi \quad [2]$$

where E represents the energy difference between the two adiabatic states to be diabaticized; $E_{\min}$ is their minimum energy difference, and ξ is an arbitrary threshold that must be adapted to the shape of each avoided crossing.

Typically, a stronger coupling will lead to a wider region I and will require a larger ξ . In this work the values of ξ were taken between 0.01 and 0.05 a.u.

Considering these constraints, the diabaticization of two adiabatic states a_i and a_j is performed by assuming an initial guess of d_j which is obtained by linking the left part of the potential energy curve of a_j and the right part of the potential energy curve of a_i by spline interpolation in the I region. The second guess diabatic curve is then obtained as:

$$d_j = a_i + a_j - d_i \quad [3]$$

For a given value of R , the $\mathbf{A}$ diagonal matrix can be built up with the two adiabatic energies. The diagonal $\mathbf{D}$ matrix containing the diabatic states can be obtained with the Adiabatic to Diabatic Transformation (ADT), which is a unitary transformation, $\mathbf{D} = \mathbf{TAT}^{-1}$. The $\mathbf{T}$ rotation matrix is defined as:

$$T = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}$$

The θ mixing angle can be extracted by simple minimization of the M merit function:

$$M = \sum_{i=1}^2 |D_{ii} - d_i| \quad [5]$$

where D_{ii} are the $\mathbf{D}$ matrix diagonal elements and d_j represents the previously estimated guessed diabatic energies. Final real diabatic states are the result of a sequence of all

possible 2x2 diabaticizations performed with all the possible pairs of states. We should remark here that the first pseudo-adiabatic states obtained will condition the choice of ξ for the following steps. Thus, the order of the sequence is to be carefully chosen in order to obtain the smoothest curves.

We call “pseudo-diabatic” states a pair of states resulting from a 2x2 diabaticization but remaining adiabatic with respect to other states. Final real-diabatic states are the product of a sequence of all the possible 2x2 diabaticizations performed with all the possible pairs of states.

Once θ is known along the whole R coordinate, $\theta(R)$ can be described as:

$$\theta(R) = \frac{1}{2} \arctan \left[a(R - b) + \frac{\pi}{2} \right] \quad [6]$$

The a and b parameters (associated with a given bending angle α) are optimized during the procedure; b corresponds to the distance of the crossing of the diabatic states, and a can be associated with the intensity of the coupling. For the fitting, our strategy implies the use of the “pseudo-adiabatic” potential energy surfaces instead of the final diabatic curves because the pseudo-adiabatic states are much simpler to fit in two dimensions. Since $\theta(R)$ is defined for each value of α , the fit of the $a(\alpha)$ and $b(\alpha)$ functions allows one to obtain the mixing angle over the whole configuration space. Then, the diabatic potential and the electronic couplings can be generated directly by applying the ADT transformation.

The validity of the procedure can be demonstrated by comparing the $\theta(R)$ function derivatives and the *ab initio* NACMEs determined using the standard procedures implemented in MOLPRO. It is found that the NACMEs calculated with our diabaticization procedure are very similar to those obtained with MOLPRO.

The *ab initio* energy corresponds to the total energy of the system for a given configuration. Since we are interested in the relative energy variation along the potential energy surface, we choose the energy of $\text{CH}_2 + \text{H}$ as the zero energy reference in order to simplify the fitting procedure. This way, the potential energy of the pseudo-adiabatic states can be decomposed in only two contributions: the internal energy of the CH_2 fragment and the interaction energy between the dissociative H atom and the CH_2 fragment,

$$V_{\text{CH}_3}(R, \alpha) = V_{\text{CH}_2}(\alpha) + V_{\text{CH}_2-\text{H}}(R, \alpha) \quad [7]$$

In the asymptotic region, the interaction between CH_2 and H vanishes and the potential energy corresponds to the internal energy of CH_2 . The energies of the CH_2 fragment can be obtained by interpolating the energies as a function of the angle. The interaction potential between H and CH_2 is then simply obtained by subtracting the energy of the CH_2 fragment.

To fit the interaction energies, we used the Reproducing Kernel Hilbert Space (RKHS) interpolation method [54], which is well suited to construct an analytical potential when the

interaction energy goes to zero for large R values and when points are sampled on a regular grid [55–56]. For a two-dimensional potential function, the RKHS analytical interaction potential can be written as [57],

$$V_{\text{CH}_2-\text{H}}(R, \alpha) = \sum_{i=1}^{N_R} \sum_{j=1}^{N_\alpha} c_{ij} q_1^{n_x, m}(R, R_i) q_2^{n_y}(y, y_i) \quad [8]$$

where q_1 and q_2 are distance-like and angle-like kernels, respectively, as defined in Ref. [54]. The kernel parameters considered in this work are $n_x=2$ and $m=5$ for the distance-like kernel to ensure a long range behaviour like R^{-6} , and $n_y=2$ to get a smooth angular behaviour. To fulfil the requirement on the angular variable range ($0 \leq y \leq 1$) and to include the wide range of α , the angular variable have been defined as $y = [1 + \cos(\frac{1}{2}\alpha)]/2$.

3 Results and Discussion

3.1 Structure of the ground electronic state

The favored D_{3h} geometry of CH_3 was determined at the MRCI and RCCSD(T)-F12 levels of theory, obtaining the CH equilibrium bond distance to be 1.0797 Å and 1.0776 Å, respectively (see Table 1). The corresponding equilibrium rotational constants are $A_e=B_e=286763.21$ MHz and $C_e=143380.29$ MHz (MRCI), and $A_e=B_e=287880.70$ MHz and $C_e=143938.92$ MHz (RCCSD(T)-F12).

In order to compare them with experimental data and to estimate the quality of the geometry, the last set was used to obtain observable ground vibrational state rotational constants according to the previously tested formula [58–59]:

$$B_0 = B_e(\text{RCCSD(T)-F12}) + \Delta B_{e\text{CORE}}(\text{RCCSD(T)}) + \Delta B^{\text{VIB}}(\text{MP2})$$

In this formula, that usually provides very accurate parameters [58–59], B^{VIB} represents the vibrational contribution to the rotational constants derived from the VPT2 a_r^i vibration-rotation $\Delta B_{e\text{CORE}} = B_e(\text{CV}) - B_e(\text{V})$ interaction parameters determined using the MP2 cubic force field (see below), and $\Delta B_{e\text{CORE}}$ is computed from $B_e(\text{CV})$ and $B_e(\text{V})$, which were calculated correlating both core and valence electrons (CV) or just the valence electrons (V) in the post-SCF process:

Using the contributions $A^{\text{CORE}} = B^{\text{CORE}} = 602.62$ MHz and $C^{\text{CORE}} = 301.31$ MHz, and $A^{\text{VIB}} = B^{\text{VIB}} = -1742.36$ MHz and $C^{\text{VIB}} = -1823.39$ MHz, the observable rotational constants are determined to be $A_0=B_0=286740.96$ MHz and $C_0=142415.92$ MHz, which are in very good agreement with the experimental rotational constants ($A_0=B_0=287201.2$ MHz and $C_0=142101.6$ MHz).

The harmonic frequencies calculated at MRCI and RCCSD(T)-F12 levels are shown in Table 1. The equation:

$$V = \omega(\text{RCCDT(T)} - \text{F12}) + \Delta V(\text{MP2}) \quad [11]$$

was employed to estimate the anharmonic fundamentals ν from the harmonic ones ω and the corresponding anharmonic contributions. The results are compared with the experimental data in Table 1. With the exception of the ν_2 out-of-plane bending mode, calculated values are in very good agreement with the available experimental data in gas phase. The ν_2 fundamental is always overestimated whereas ω_2 is always underestimated. It is noted, however, that for the ν_2 out-of-plane bending mode, the negative anharmonicity observed experimentally [11] is qualitatively predicted by our calculations, although the level of theory (MP2) employed to describe the anharmonic effects is not sufficient to obtain an accurate result. This frequency is really dependent on the selection of the active space in the multiconfigurational calculations. If only seven valence orbitals are included, which is the default option, ω_2 decreases to 291 cm^{-1} . At least, a set of eight orbitals is needed to reach the value of $\omega_2 = 493 \text{ cm}^{-1}$.

3.2 Excited electronic states

All the electronic states involved in the photodissociation of the methyl radical from the $3s$ and $3p_z$ Rydberg states are included in the set of 8 electronic states considered in the SA-CASSCF procedure. Their asymptotes correlate with the electronic states of methylene (CH_2), which were determined at the same level of theory as those of CH_3 and are shown in Table 2 and compared with experimental data [2,60–61]. By ignoring the couplings, the adiabatic correlation diagram between the bound states of methyl and methylene, presented in Fig. 2, is in good agreement with the work of Yu et al. [43]. We should remark here that the B_2 contribution of the $3p_{x,y}(E)$ Rydberg state (doubly degenerate), correlating with a highly excited state of CH_2 , is shown only for completeness. Unlike the A_1 contribution, the B_2 state is uncoupled to the states involved in the dissociation processes.

The calculated vertical excitation energies of the different states of the methyl and methylene radicals are shown in Table 2 and compared with experimental values and with the “adiabatic” values. It is noted that the MRCI vertical excitations are calculated as the energy difference between the energy minimum of the ground electronic state and the different excited electronic states at the optimized geometry of the ground state energy minimum for all the states. In the case of the MRCI adiabatic excitations, they are calculated as the energy difference between the ground and the excited state, both in their corresponding equilibrium geometry. The analytical values (fit vertical excitations) obtained by the RKHS potential are also included in order to show the quality of the fitting procedure. The agreement between *ab initio* vertical excitations and the RKHS ones is excellent and compares well with experimental values for CH_3 .

For methylene, the comparison between the MRCI vertical excitations and the corresponding experimental values is poorer in some cases, since the equilibrium HCH bending angle varies significantly for some of the excited electronic states. In those cases where the equilibrium bending angle is similar for both the ground and the corresponding excited state (like in the b^1B_1 and $3p^3B_1$ states), comparison between the *ab initio* and the

experimental vertical excitations is very good. For the other cases, comparison with experimental values greatly improves when the correct equilibrium angle in the excited states is considered, as shown by the values of the fit vertical excitation column of the table. These results indicate that both the *ab initio* calculations and the analytical potentials are precise enough to describe the system correctly.

Both the $3s$ Rydberg state and the A_1 valence state are represented in Fig. 3. The angular dependence of the A_1 state shows that there is a barrier at 180° that separates two valleys around the angular regions of 100° and 250° . Since the well of the $3s$ Rydberg state is located at 120° , dissociation along the lower angle valley is favored, at least for the lower initial vibrational states of CH_3 in the $3s$ state. In addition, the crossing between the $3s$ and A_1 states occurs at rather low energies of the $3s$ surface along the angular range, not very far from the energy minimum, as shown in the contour plots. As a result, when low vibrational states of CH_3 are prepared in the $3s$ state, the amount of energy available for the dissociation fragments will be rather low, leading to rovibrationally cold CH_2 fragments. In particular, bending excitation of the CH_2 fragment is expected to be very low, since the available energy will not be enough as to overcome the angular barrier of the A_1 valence state.

This picture is consistent with the narrow distribution of rovibrational excitation found experimentally for the CH_2 fragment produced by photodissociation of the $\text{CH}_3(\nu=0)$ radical in the $3s$ state [39]. Based on the angular dependence of the potentials shown in Fig. 3, it is predicted that in order to get CH_2 fragments with significant bending excitation in the photodissociation of the methyl radical from the $3s$ Rydberg state, the energy of the vibrational state of CH_3 initially prepared should be above the energy of the angular barrier found in the A_1 valence state at 180° .

A rather different situation is found for the potential energy surfaces of the $3p_z$ Rydberg and B_1 valence states, displayed in Fig. 4. On the one hand, the angular barrier at 180° in the B_1 valence state is much lower in energy than that in the A_1 valence state, requiring a remarkably lower amount of energy to be overcome. On the other hand, the crossing between the two potential energy surfaces occurs at higher energies in the $3p_z$ surface along the whole angular range, far away from the minimum, in comparison with the $3s$ state. Actually, as can be seen in the figure, the energy minimum of the $3p_z$ state lies above the top of the angular barrier. Thus, even the lowest vibrational levels of CH_3 in the $3p_z$ state are energetically above the angular barrier, implying that a significant rovibrational excitation (particularly in the bending mode) of the CH_2 fragment is expected. Indeed this is again consistent with the experimental finding of a broad internal energy distribution of the CH_2 fragment produced upon predissociation of the $\text{CH}_3(\nu=0)$ radical in the $3p_z$ state through the B_1 valence state, $\text{CH}_3(\nu=0) \rightarrow \text{CH}_2(\text{b } ^1B_1) + \text{H}(^2S)$ [39].

The electronic coupling between the $3s$ Rydberg state and the A_1 valence state is plotted in both the radial and angular modes in Fig. 5, and the corresponding coupling between the $3p_z$ state and the B_1 valence state is shown in Fig. 6. While the couplings are rather localized along the radial coordinate, as found in the previously reported one-dimensional representation [38,39], they extend along the whole angular range. Most interestingly, it is

found that the width of the couplings in the R coordinate depends strongly on the bending angle, particularly in the case of the coupling between the $3s$ and A_1 states.

For the lowest vibrational states of CH_3 both in the $3s$ and $3p_z$ Rydberg states, the relevant angular region for the couplings is that around 120° , where the minima of the bound potential surfaces are localized. In this angular region the $3s$ Rydberg state displays a stronger and wider coupling than the $3p_z$ state, which is consistent with the splittings observed in the avoided crossing in the adiabatic representation. However, as vibrational excitation of CH_3 increases, particularly in the bending mode, regions of the couplings at higher angles may become important. Since the couplings at those regions are remarkably intense, an increasingly faster predissociation process is predicted upon increase of the CH_3 bending excitation, especially in the case of the $3p_z$ Rydberg state.

In order to interpret the differences in the photodissociation dynamics between the $3s$ and $3p_z$ Rydberg states, one should also discuss the impact of the zero point vibrational energy (ZPVE). With this aim, the vibrational harmonic frequencies of both $3s$ and $3p_z$ Rydberg states were calculated at MRCI level of theory. The results, as well as some structural basic properties, are presented in Table 3.

For both states, few experimental values are available. The $3s$ Rydberg state has not been characterized experimentally and only approximate values derived for two modes are available, making difficult to use them to assess the quality of the calculations that provide results far away from the estimations. For example, Westre et al. [29] have analyzed the structure and dynamics of vibronic levels in the methyl radical Rydberg $3s$ state using far-ultraviolet resonance Raman spectroscopy. The out-of-plane bend frequency, ν_2 , in the Rydberg $3s$ state was determined to be 1094 cm^{-1} . The symmetric stretching frequency, ν_1 , was estimated to be 2040 cm^{-1} . Although we provide only computed harmonic contributions, calculations disagree with these estimations.

However, the $3p_z$ state has been better characterized. Available experimental data comes from Hudgens et al. [26] and Zhang et al. [32]. They provide band center positions for ν_1 and ν_2 of 2931 cm^{-1} and 1323 cm^{-1} , respectively, whereas the values corresponding to the degenerate modes were estimated from the isotope shifts of the electronic ground state to be 3114 cm^{-1} and 1428 cm^{-1} , respectively. With the exception of ν_3 , calculations and experimental data are in very good agreement. For ν_3 , divergences can be related to anharmonic effects.

From the present *ab initio* frequencies calculation, the ZPVE of the $3s$ and $3p_z$ Rydberg states lies at 0.75 eV and 0.85 eV over the minima, respectively. This large amount of vibrational energy is sufficient to overcome the value of the crossing in the case of the $3s$ and A_1 states. This favors a fast dissociation process. In the case of the $3p_z$ Rydberg state, the amount of vibrational energy is even bigger, but not enough to overcome the energy of the crossing with the B_1 state. This fact, along with a weaker coupling, causes a slower predissociation process than in the case of the $3s$ Rydberg state.

4 Conclusions

The ground and excited electronic states involved in the photodissociation of the CH₃ radical have been investigated through highly correlated *ab initio* methods. More specifically, the excited states studied were the 3*s* and 3*p_z* Rydberg states, and the *A*₁ and *B*₁ valence states that cross with them, respectively. Non-adiabatic couplings between the crossing states were also calculated. Two degrees of freedom of CH₃, namely the C-H dissociative coordinate and the HCH bending angle, were considered in the calculation of the different potential energy surfaces and electronic couplings, giving rise to the first two-dimensional *ab initio* representation of the above electronic states of CH₃. Calculated spectroscopic constants and frequencies for the ground and the bound excited states were compared with available experimental data. Very good agreement was found in general, which assesses the good quality of the potential energy surfaces reported.

The dependence of the potential energy surfaces and couplings on the two coordinates, and particularly on the bending angle, is analyzed and discussed in relation to the possible dissociation pathways. The computed *ab initio* surfaces explain consistently the recent experimental findings observed for CH₃ photodissociation from low vibrational states in the 3*s* and 3*p_z* Rydberg states. Based on the present potential energy surfaces, some predictions are also made regarding CH₃ photodissociation from higher excited initial vibrational states. Thus, the *ab initio* surfaces reported in this work are viewed as a significant advance for a more precise theoretical characterization of the CH₃ radical molecule.

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Figure 1.
Schematic view of the coordinates used to build the 2D-potentials

Figure 2.
Correlation diagram between the adiabatic electronic states of CH_3 and CH_2 .

Figure 3.

Potential energy surfaces of the $3s$ Rydberg state and the dissociative A_1 valence state. (Top) Three-dimensional representation, (middle) contour plot of the $3s$ Rydberg state, (bottom) contour plot of the valence A_1 state. The black solid lines indicate the intersection of both states.

Figure 4.

Potential energy surfaces of the $3p_z$ Rydberg state and the dissociative B_1 valence state. (Top) Three-dimensional representation, (middle) contour plot of the $3p_z$ Rydberg state, (bottom) contour plot of the B_1 valence state. The black solid lines indicates the intersection of both states.

Fig. 5.
Electronic couplings between the $3s$ Rydberg state and the dissociative A_1 valence state.
(Top) Three-dimensional representation, (bottom) contour plot.

Fig. 6.
Electronic couplings between the $3p_z$ Rydberg state and the dissociative B_1 valence state.
(Top) Three-dimensional representation, (bottom) contour plot.

Table 1

Structural and spectroscopic parameters corresponding to the ground electronic state of the CH₃ radical. See the text for details of the different calculations.

	MRCI	CCSD(T)-F12		MRCI	CCSD(T)-F12	
R_e (C-H) (Å)	1.0797	1.0776	E (a.u.)	-39.762422	-39.773407	
Rotational constants (in MHz)						
	B_e MRCI ^a	B_e CCSD(T)-F12	B_0 Estimated	Exp.	[Ref]	
$A=B$	286763.21	287880.70	286740.96	287137.92	[11,14]	
C	143380.29	143938.92	142415.92	142162.18 142184.07	[11] [14]	
Fundamental frequencies (in cm^{-1})						
Symmetry	Assignment	MRCI ^a ω	CCSD(T)-F12 ω	ν	Exp.	[Ref]
a_1'	CH stretch	3111	3122	3008	3004.43±0.02	[5–9]
a_2''	out-of-plane bending	493	508	692	606.493	[10–13]
e'	CH stretch	3291	3304	3163	3160.821	[14–20]
e'	CH deformation	1418	1422	1394	1396-1403	[21–22]
ZPVE (eV)		0.81	0.81	0.79		

^{a)} Active space of 11 orbitals (6a 1+3b 1+2b 2)

Table 2

Theoretical and experimental excitation energies (in eV) from the ground to the excited electronic states of the methyl (CH_3) and methylene (CH_2) radicals. See the text for details of the different calculations.

<i>Methyl radical (CH_3)</i>						
D_{3h}	C_{2v}	Valence/Rydberg character	MRCI vertical excitation	Fit vertical excitation	MRCI adiabatic excitation	Exp. [Ref]
$\tilde{X}^2A_2''$	$\tilde{X}^2B_1$	Valence	0.0	0.0	0.0	0.0
$3s^2A'$	2A_1	Rydberg	5.91	5.93	5.69	5.73 [1–2,24,29,31,37]
$3p_{xy}^2E'$	$^2(A_1+B_2)$	Rydberg	7.03	7.02	5.87	
$3p_z^2A_2''$	2B_1	Rydberg	7.66	7.66	7.55	7.43 [26–30,32–33]
<i>Methylene radical (CH_2)</i>						
C_{2v}	MRCI vertical excitation		Fit vertical excitation	Fit adiabatic excitation		Exp. [Ref]
X^3B_1	0.0		0.0	0.0		0.0
a^1A_1	0.85		0.85	0.43		0.39 [2]
b^1B_1	1.45		1.45	1.33		1.43 [2]
c^1A_1	3.28		3.28	2.48		2.25 [60]
1^3A_1	6.48		-	-		-
3^1A_1	6.70		-	-		-
$3p^3B_1$	7.69		7.69	6.63		7.95 [61]

Table 3

Adiabatic excitation energies (E), equilibrium bond distances (R_e), rotational constants ($A_e=B_e, C_e$) and harmonic frequencies (ω) of the CH_3 $3s$ and $3p_z$ Rydberg states calculated with MRCI/AVTZ^a.

		Rydberg 3s		Rydberg 3p _z	
E (eV)		5.69		7.55	
R _e (C-H) (Å)		1.1153		1.0897	
A _e = B _e (MHz)		268739.45		281548.66	
C _e (MHz)		134369.73		140774.33	
Harmonic frequencies (ω in cm ⁻¹)					
		Rydberg 3s		Rydberg 3p _z	
		MRCI	Exp. [Ref]	MRCI	Exp. [Ref]
ω (a ₁ ')	CH stretch	2520	2040 ([*]) [29]	3037	2931 [26,32]
ω (a ₂ '')	out-of-plane bending	1422	1094 [29]	1339	1323 [26,32]
ω (e')	CH stretch	2802	-	3222	3114 ([*]) [32]
ω (e')	CH deformation	1277	-	1427	1428 ([*]) [32]
ZPVE	0.75 eV			0.85 eV	

^{a)}Space active of 11 orbitals (6a₁+3b₁+2b₂)

(*) Estimated values