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ABSTRACT

Bromine atom (Br) reactions lead to ozone depletion in the troposphere and stratosphere. Photodegradation of bromocarbons is one of the main sources of bromine atoms in the atmosphere. Here, we use high-level *ab initio* methods, including spin-orbit effects, to study the photodissociation of the CH₂Br radical. All possible fragmentation pathways, namely CH₂Br + *hν* → CH₂ + Br, HBr + H, and CBr + H₂, have been analyzed. Potential-energy curves of the ground and several excited electronic states along the corresponding dissociating bond distance of each pathway have been calculated. Considering the actinic fluxes of solar irradiation in the troposphere and in the stratosphere in the relevant range of frequencies, it is found that the first five excited states of CH₂Br can be accessed from the ground state. Analysis of the potential curves shows that the pathways producing CH₂ + Br and HBr + H can proceed through a fast direct dissociation mechanism, while the pathway leading to CBr + H₂ involves much slower dissociation mechanisms like internal conversion between electronic states, predissociation, or tunneling through exit barriers. The main implications are that the two faster channels are predicted to be dominant, and the slower pathway is expected to be less relevant. The tropospheric and stratospheric solar actinic fluxes also allow for further dissociation of the HBr and CBr fragments, generating additional Br atoms, provided that they survive possible collisions with other atmospheric reagents. Finally, we discuss the possible effect of each of the three CH₂Br dissociation pathways on the depletion of atmospheric ozone.

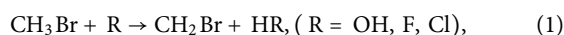
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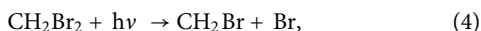
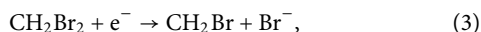
I. INTRODUCTION

The photochemistry of radicals and reactive intermediates is particularly important in atmospheric and interstellar chemistry.¹ Reactive intermediates of the family of halocarbon radicals play an active role in gas phase reactions with ozone to produce carbon monoxide, forming adducts with N- and O-bearing molecules, or producing the functionalization of aromatic molecules.^{2,3} Here, we specifically investigate the photodissociation of the CH₂Br radical and its relevance for atmospheric chemistry. Among several other reactions in the atmosphere, it is well known the important role of CH₂Br as a reactive intermediate in the formation of the

simplest Criegee intermediate, CH₂OO, starting from CH₂Br₂ in the presence of oxygen (CH₂Br + O₂ → CH₂OO + Br),^{4,5} which is of great relevance to atmospheric and combustion chemistry. Another typical reaction occurring in the atmosphere due to the abundance of molecular oxygen is the formation of the peroxy radical, CH₂Br + O₂ + M → CH₂BrO₂ + M, where M is a third body.⁶

The CH₂Br radical can be produced through different reactions, some of them starting from either CH₃Br, CH₂Br₂, or CH₂BrI,⁵⁻⁸

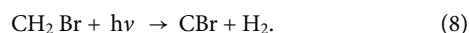
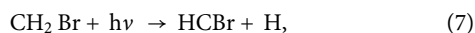
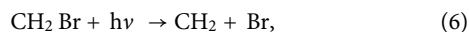




Theoretical studies on CH_2Br , and particularly *ab initio* calculations, are rather scarce, probably due to the fact that species containing heavy halogen atoms like Br are computationally demanding. Previous *ab initio* calculations determined the adiabatic ionization energy and electron affinity of CH_2Br and found a nearly planar equilibrium geometry in the ground electronic state.⁹ Later works^{8,10} calculated ionization energies, inversion barriers, rotational constants, and vibrational spectra in the ground electronic state using density functional theory (DFT) and different *ab initio* methods. Further calculations on the equilibrium structure,^{11,12} inversion barrier to planarity,¹³ and vibrational frequencies⁵ of CH_2Br in the ground electronic state were reported. To the best of our knowledge, only one *ab initio* study has reported potential-energy curves (PECs) of the ground and low-lying excited electronic states of CH_2Br along the C–Br bond distance at the complete active space self-consistent field (CASSCF) level of theory.⁶

The CH_2Br radical was first observed in electron impact experiments,¹⁴ and matrix infrared (IR) spectroscopy studies^{15,16} provided some vibrational frequencies. Electron spin resonance experiments¹⁷ supported the planarity of CH_2Br . From gas phase photoelectron spectroscopy, the adiabatic ionization energy was obtained,^{9,18} and the rotationally resolved spectra of the radical ground vibrational state were measured by far-IR spectroscopy.¹⁹ Millimeter wave^{20,21} and Fourier transform microwave²² spectroscopic experiments in the ground electronic state were reported later on. Recently, the first IR high-resolution spectra on the symmetric CH stretch excitation (ν_1) of CH_2Br in the electronic ground state have been published.⁵ The rate constants of the reaction of CH_2Br with O_2 were measured at different atmospheric temperatures in the range of 220–450 K.²³ Regarding the excited electronic states of CH_2Br , several absorption bands to different states have been measured, like the bands found at ~250 and 280 nm,²⁴ at ~230 nm,²⁵ and at 228.7 and 239.5 nm.¹¹

The present work aims to theoretically investigate the photolysis of CH_2Br in the atmosphere through all the possible fragmentation pathways. More specifically, photodissociation of CH_2Br can occur through the dissociation pathways,



The above-mentioned pathways were investigated using highly correlated *ab initio* methods including spin–orbit effects, by calculating

the PECs of the ground and several excited electronic states along the corresponding dissociation coordinates. Pathways (6)–(8) are all of atmospheric relevance. In particular, pathway (6) may contribute to increase the budget of atomic Br in different regions of the atmosphere. It is well known that atomic halogens ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are among the main causes of the depletion of ozone ($\text{X} + \text{O}_3 \rightarrow \text{XO} + \text{O}_2$) in the stratosphere and troposphere^{26,27} and have an indirect cooling effect on climate.²⁸ While CH_3Br formed by marine biological activity is one of the main sources of atomic bromine in the atmosphere,^{26,27} pathway (6) may also be a relevant contribution in the atmospheric regions where radiation is abundant enough. Pathways (7) and (8) are also interesting because they produce other bromocarbon radical species that can be intermediates in several atmospheric chemical processes and cycles.

Our study intends to elucidate how and in which conditions CH_2Br photodissociation may affect atmospheric chemistry, particularly in the stratosphere and troposphere. Specific objectives of this study are (i) to establish the most likely photodissociation pathways and mechanisms through which CH_2Br is expected to disappear in the atmosphere, (ii) to predict the feasibility of producing atomic bromine through pathway (6) that could impact ozone depletion, and (iii) to investigate the possibility to form new HCB r and CBr radicals through pathways (7) and (8).

II. THEORETICAL METHODOLOGY

In this work, all the calculations were performed with the MOLPRO package,²⁹ and the full electron ANO-RCC-VTZP basis set was considered for all atoms. The dissociation pathways (6)–(8) of the CH_2Br radical were explored by computing one-dimensional PECs in several electronic states with high-level *ab initio* methodologies. For each of these pathways, about 40 points were considered between 1 and 8 bohrs along the corresponding reaction coordinates, namely C–Br, C–H, and C–H₂. For each of the different points along the reaction coordinate, the geometry in the remaining five coordinates of CH_2Br was optimized (i.e., the equilibrium geometry of minimum energy in those coordinates was obtained) in the ground electronic state at the complete active space perturbation theory of second order (CASPT2) level³⁰ with a minimal active space. These equilibrium geometries optimized in the ground state are also used in the calculation of the excited state curves. The determination of the global minimum equilibrium geometry and harmonic frequencies was also carried out at this level. Once the equilibrium geometries of the three reaction pathways were obtained, the potential-energy curves were finally computed for the ground and excited states at the CASSCF and multireference configuration interaction (MRCI) levels,^{31,32} including spin–orbit effects. The CH_2Br radical is a planar molecule, and in order to keep the same symmetry group for all the pathways, all calculations were performed within the C_s symmetry point group.

The present study extends the pioneering work of Li and Francisco⁶ by including the photodissociation pathways (7) and (8) in addition to the previously investigated pathway (6). A higher level of theory is currently applied in this work compared to that of Li and Francisco,⁶ where the PECs were computed at the CASSCF level without considering the spin–orbit coupling. Therefore, the present

study is expected to be both accurate and thorough enough to provide valuable insight and understanding into the effect of CH_2Br photolysis on atmospheric chemistry.

Due to the presence of a Rydberg state strongly affecting the Franck–Condon (FC) region of this system, it becomes impossible to find a single active space able to correctly describe all the fragmentation routes for all the electronic states. Therefore, each channel has been treated in a different way. For the elimination of the Br atom [pathway (6)], two different active spaces have been considered. At the CASSCF level, the step where the orbitals are optimized, a first calculation was performed, including the Rydberg orbital, leading to an active space of seven electrons in seven orbitals (15–19 a' and 5–6 a'' orbitals). 17 electronic states were considered in these calculations, namely 9 states of $^2A'$ symmetry, 5 of $^2A''$, 1 of $^4A'$, and 2 of $^4A''$. In order to capture more correlation, the active space was then slightly augmented to 12–19 a' and 5–6 a'' orbitals at the MRCI level, where 13 electronic states were calculated (5 states of $^2A'$ symmetry, 5 of $^2A''$, 1 of $^4A'$, and 2 of $^4A''$). With this calculation, however, the description of the PECs is not smooth along all C–Br distances considered, and the description of the asymptotic region fails. Since Rydberg orbitals are not expected to play a role in the asymptotic region, another calculation was performed without including the Rydberg orbital using an active space of 12–17 a' and 5–6 a'' orbitals in order to obtain a good description of the asymptotic region. In this case, the number of states considered at the CASSCF and MRCI levels was reduced accordingly to 4 states of $^2A'$ symmetry, 5 of $^2A''$, 1 of $^4A'$, and 2 of $^4A''$. Since two different active spaces are considered, total energies cannot be directly compared. To obtain the final curves, the PECs calculated with the smaller active space were shifted to match the other set of PECs just before the asymptotic region. The procedure applied is discussed in more detail in Sec. 1 of the supplementary material (Fig. S1).

Regarding the elimination of atomic and molecular hydrogen [pathways (7) and (8), respectively], the active space (including 12–19 a' and 5–6 a'' orbitals) was found to be stable to fully describe the fragmentation when considering 5 states of $^2A'$ symmetry, 5 of $^2A''$, 1 of $^4A'$ state, and 2 of $^4A''$, using the same active space at the CASSCF and MRCI levels. Finally, for all fragmentation pathways, spin–orbit matrix elements were calculated from the MRCI electronic wavefunctions using the Breit–Pauli method implemented in MOLPRO,³³ and the eigenvalues of the full spin–orbit matrix that include the spin-free electronic states above-mentioned are computed to give the final spin–orbit states of the system.

III. RESULTS AND DISCUSSION

A. Geometrical and energetic properties

Figure 1 displays the global minimum equilibrium geometry optimized in the ground electronic state for CH_2Br , showing the equilibrium distances and angles. These distances and angles are also collected in Table I, where they are compared with the values calculated in previous *ab initio* studies for CH_2Br and with experimental values. Very good agreement is found between the present and the previously computed geometries, as well as with the experimental values. Our calculations indicate that the equilibrium structure of CH_2Br is planar. It is known that the degree of planarity found for the radical depends on the level of theory of the *ab initio*

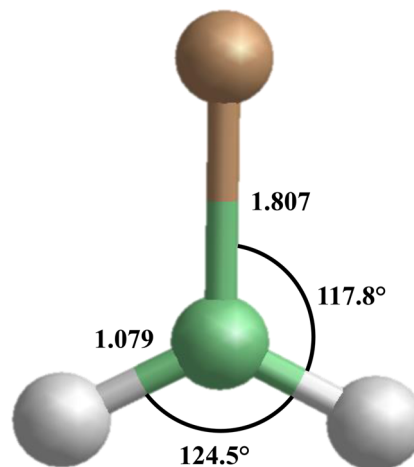


FIG. 1. Distances (in Å) and angles (in degree) associated with the equilibrium geometry optimized in the ground electronic state for CH_2Br .

method applied,^{6,8,10} as can be seen in Table I. However, highly correlated levels of theory typically find planar or very nearly planar equilibrium geometries.^{6,10}

The harmonic frequencies of the six vibrational modes of CH_2Br were also calculated, collected, and compared with previous theoretical and experimental frequencies in Table I. The present frequencies are very similar in general to the earlier theoretical ones. An exception to this agreement is the imaginary frequency obtained for the ν_4 mode in the calculation of Li and Francisco.¹⁰ It is noted that considering a planar geometry (C_s) in our calculations leads to a real frequency for the umbrella mode, which confirms that the geometry of the PEC minimum is indeed planar. The current theoretical frequencies are also in very good agreement with the experimental ones, being closer (like for ν_1 and ν_3) or similarly close (like for ν_2 and ν_6) to them as the previous theoretical frequencies. The adiabatic ionization energy calculated here (see Table I) is somewhat smaller than the experimental and previously computed ones, but it is still very close to all of them. The above-mentioned comparisons assess the accuracy of the present calculations for the electronic ground state of the CH_2Br radical. The bromine spin–orbit splitting has also been calculated and is collected in the last row of Table I. The value obtained compares very well with the experimental one.

In Table II, the vertical excitation energies (VEEs) for the first excited states of CH_2Br from the minimum of the ground state $\tilde{X}^2A'$ are presented and compared with those calculated by Li and Francisco.⁶ The present energies are very similar to (although slightly lower than) the previous ones for the first three excited states. Much larger differences appear for the next two excited states, for which the present energies are substantially lower than those of Li and Francisco.⁶ This result indicates that the spin–orbit coupling becomes increasingly pronounced as the energy of the states increases. The VEEs are consistent with the absorption bands observed for CH_2Br . Indeed, the energies of Table II associated with 281 and 260 nm are consistent with the bands measured at 280 and ~ 250 nm²⁴ and would correspond to transitions to the first and

TABLE I. Equilibrium geometries, harmonic frequencies, and adiabatic ionization energy of the electronic ground state of CH₂Br, and Br spin–orbit splitting calculated in this work, and comparison with previous theoretical and experimental data.

CH ₂ Br(C _s) 1 ² A'	(This work)	Theory ^a	Theory ^b	Theory ^c	Experiment
r _{C-H} (Å)	1.079	1.076	1.075	1.076	1.086 ^d
r _{C-Br} (Å)	1.807	1.850	1.851	1.851	1.845 ^d
HCH (deg)	124.5	123.8	124.1	124.1	124.0 ^d
HCB _r (deg)	117.8	118.1	117.9	117.9	118.0 ^d
CBrHH (deg)	180.0	172.9	178.5	179.5	
ν ₁ (cm ⁻¹) CH s-stretch (a')	3154	3176	3185		3053 ^e
ν ₂ (cm ⁻¹) CH ₂ scissors	1408	1416	1407		1356 ^f
ν ₃ (cm ⁻¹) CBr stretch	654	724	718		693 ^f
ν ₄ (cm ⁻¹) CH ₂ Br umbrella	198	140	52i		368 ^f
ν ₅ (cm ⁻¹) CH a-stretch (a'')	3310	3325	3341		
ν ₆ (cm ⁻¹) CH ₂ rock	939	946	937		953 ^f
Ionization energy (eV)	8.30	8.45	8.53		8.61 ^g
Br spin–orbit splitting (cm ⁻¹)	3792				3685 ^h

^aReference 8, unrestricted quadratic configuration interaction (UQCISD) calculations using a 6-311 + +G(3df,3pd) basis.^bReference 10, coupled-cluster [CCSD(T)] calculations using a 6-311 + +G(3df,3pd) basis.^cReference 6, coupled-cluster [CCSD(T)] calculations using a 6-311 + +G(3df,3pd) basis.^dReference 19.^eReference 5.^fReferences 16 and 18.^gReferences 9 and 18.^hReference 38.**TABLE II.** Computed vertical excitation energies (in eV) for the first excited states of CH₂Br with respect to the minimum of the ground state 1²A'. The present energies are compared to previous *ab initio* MRCI results not considering spin–orbit coupling. In parenthesis, the wavelength (in nm) associated with each calculated energy.

State	This work	Theory ^a
1	...	...
2	4.42 (281)	4.45 (279)
3	4.76 (260)	4.80 (258)
4	5.40 (230)	5.62 (221)
5	5.75 (216)	6.96 (178)
6	6.11 (203)	7.87 (158)

^aReference 6, MRCI calculations.

second excited states, respectively. Similarly, the energy of Table II associated with 230 nm is consistent with the bands found at ~230 nm²⁵ and at 239.5–228.7 nm,¹¹ corresponding to a transition to the third excited state.

B. Potential-energy curves of the fragmentation pathways

The adiabatic PECs of CH₂Br along the C–Br and C–H bond distance and along the C–H₂ distance are shown for the ground and several excited states in Figs. 2–4, respectively. The PECs of Fig. 2 are obtained by matching the curves calculated using two different active spaces along the C–Br distance, as commented in Sec. II and described in detail in the supplementary material. The upper panel of Figs. 3 and 4 shows the MRCI PECs, including the spin–orbit

coupling. The symmetry of these PECs is difficult to assign when the spin–orbit coupling is considered. For this reason, in the lower panel of the figures, we present the MRCI PECs obtained without including the spin–orbit coupling. In this case, the symmetry of the PECs can be assigned both in the FC and in the asymptotic region, providing a clue on the symmetry of some of the spin–orbit PECs in the upper panel. The PECs with and without spin–orbit coupling are very similar in shape in the FC region and at short distances. The 13 MRCI states found when the spin–orbit coupling is not considered split into 16 doubly degenerated spin–orbit states (giving a total of 32 states; in Figs. 2–4, most of the MRCI and spin–orbit states are shown). The conversion of the crossings between uncoupled states in the spin-free representation into new avoided crossings when they become spin–orbit coupled is what reshapes the spin–orbit PECs.

In Fig. 2, the PECs of the first and second excited states exhibit a shallow well. This is at variance with the repulsive curves obtained by Li and Francisco.⁶ However, in the FC region, mainly the repulsive part of the PEC of the first excited state is accessed. The shallow well of the second excited state can be accessed from the ground state in the FC region, but the very low exit barrier displayed by the PEC around 4 bohrs indicates that dissociation in this state should be easy. Therefore, despite the existence of shallow wells, the shape of the PECs of these two excited states suggests that they will behave in practice as repulsive states, and upon excitation, the main dynamical mechanism will be the direct fragmentation of the radical into the CH₂ and Br products.

The excited states higher than the two first ones display an essentially repulsive shape, so upon excitation to these states

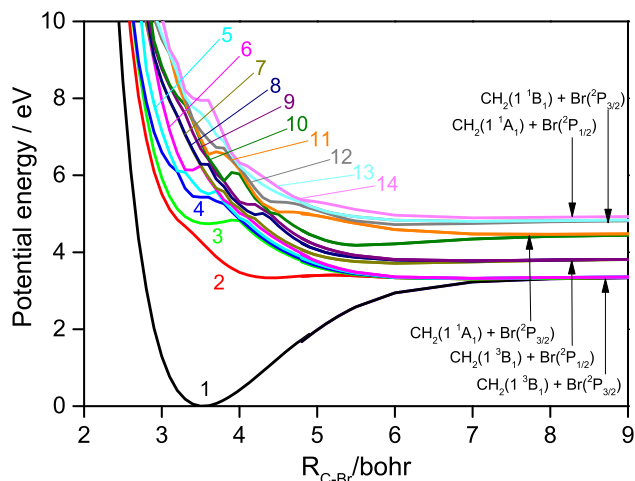


FIG. 2. Adiabatic potential-energy curves of the ground and excited electronic states of CH_2Br along the C–Br bond distance calculated at the MRCI level including the spin–orbit coupling. The curves are calculated by including the Rydberg orbital in the active space for $R_{\text{C-Br}} \leq 4.9$ bohrs and by removing the Rydberg orbital from the active space for $R_{\text{C-Br}} \geq 4.7$ bohrs and then matching the two parts of the curves. See the supplementary material for details.

(at energies >5.5 eV, see Table II), direct fragmentation of the radical will be the leading mechanism. A relatively large density of states is found as a consequence of the splitting due to the spin–orbit coupling. The implication of this high density of states is that several electronic states (those with oscillator strength) can be excited simultaneously at a given energy. The curves display several low exit barriers (even more than one in the same curve) produced by avoided crossings between the PECs. It is noted that another avoided crossing appears to occur around 3.4 bohrs between the first and second excited states. Therefore, all the states seem to be strongly coupled between them. Therefore, upon excitation to these states above 5.5 eV (<225 nm) and due to the several non-adiabatic and spin–orbit couplings connecting the different excited PECs, dissociation of CH_2Br on various PECs is expected to occur, producing CH_2 and Br fragments in a variety of electronic states and with a rather broad distribution of translational energies.

Focusing now on the spin–orbit PECs of Fig. 3(a) (C–H dissociation), we find that, in contrast to those of Fig. 2 (C–Br dissociation), all the excited states are bound with more or less deep wells, with one or more exit barriers in several states, which are the result of numerous avoided crossings between the curves. Interestingly, the first excited state displays a very shallow well, which implies that upon excitation to this state, direct dissociation into HCB and H fragments will be the dominant mechanism. The wells of the first excited states are not far from each other, typically being partially embedded below the asymptote of the immediately lower electronic state. This situation suggests that, upon excitation of a given excited state, relaxation through internal conversion to rovibrationally excited states of the lower electronic states may occur. Predissociation between different electronic states is also expected to be likely due to the nonadiabatic couplings associated with the several avoided crossings found in the PECs. Tunneling through

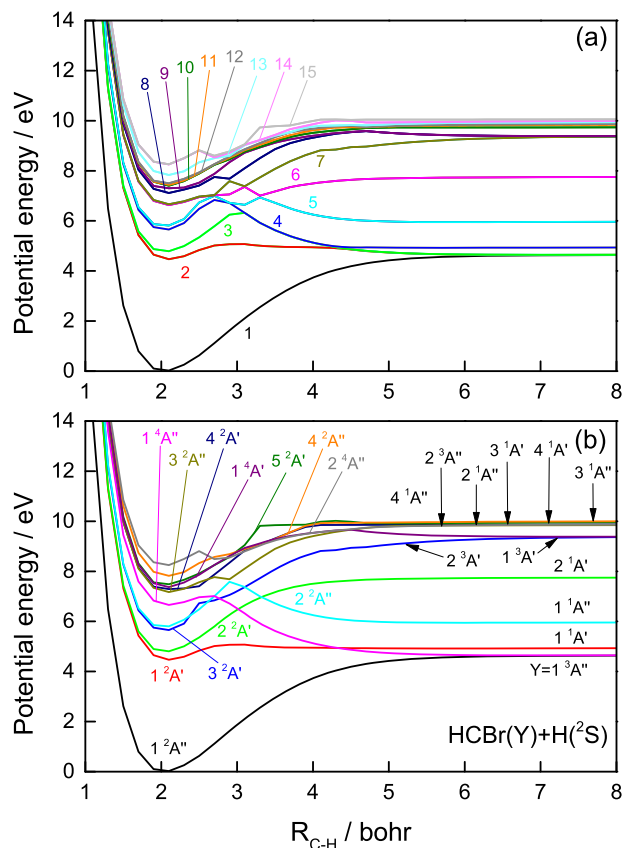


FIG. 3. Adiabatic potential-energy curves of the ground and excited electronic states of CH_2Br along the C–H bond distance, calculated at the MRCI level (a) including and (b) not including the spin–orbit coupling.

the exit barriers is another possible and likely dissociation mechanism, especially for the elimination of the light H atom. Fluorescence to the ground state is a nondissociating possibility to reach the lowest state from those excited states radiatively coupled to it. Actually, the dynamics is expected to consist of a combination of the above-mentioned mechanisms, i.e., after exciting a given state, the internal conversion will populate several lower states where predissociation and tunneling will cause the fragmentation of CH_2Br into HCB and H. It is noted that our spin–orbit MRCI calculations, the same as the MRCI results of Burrill and Grein,³⁴ found that the energy location of the asymptotes of the different electronic states in Fig. 3 changes substantially with the HCB angle (see Fig. S2 and the discussion in Sec. 2 of the supplementary material), which may affect the possible dissociation mechanisms upon the C–H bending vibration.

Similarly to Fig. 3, the excited state spin–orbit PECs of Fig. 4 (C–H₂ dissociation) are all bound, also displaying one or more exit barriers as a result of several avoided crossings between different curves. The main differences are that in Fig. 4, the wells are generally deeper, and the exit barriers are typically higher than in the PECs of Fig. 3. This is particularly the case with the two first excited states. Interestingly, the ground state also exhibits a rather high exit bar-

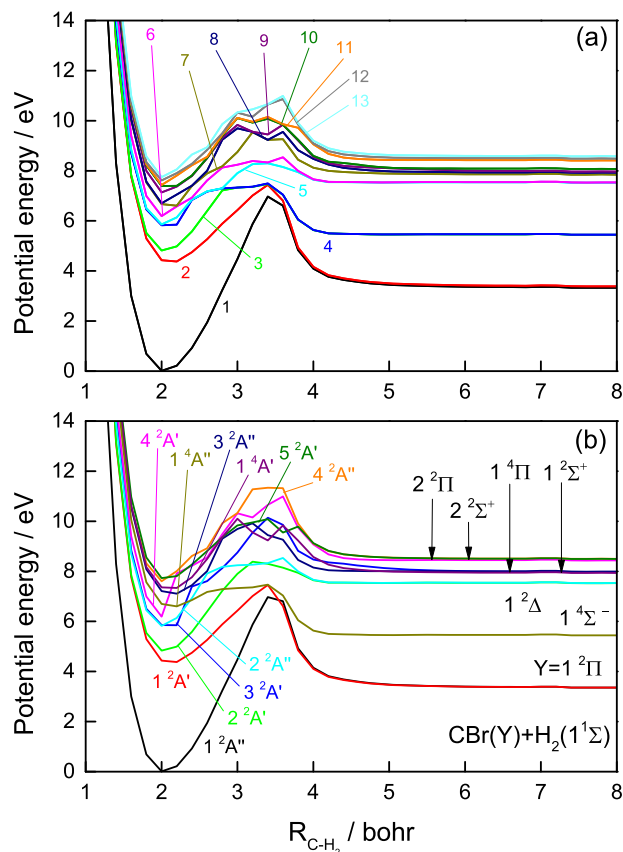


FIG. 4. Adiabatic potential-energy curves of the ground and excited electronic states along the C–H₂ distance (the distance between C and the center of mass of H₂), calculated at the MRCI level (a) including and (b) not including the spin–orbit coupling.

rier. Therefore, upon excitation to the first excited states, a similar dynamics to that discussed for the PECs in Fig. 3 is expected.

According to the PECs depicted in Fig. 4, relaxation by internal conversion to lower electronic states is a very likely mechanism. The difference between the curves in Fig. 3 is that now internal conversion to highly excited rovibrational states of the ground electronic state is possible. Such excited rovibrational states could dissociate by tunneling through the ground state exit barrier. However, this barrier is much higher than the ground state thresholds for both Br-atom and H-atom eliminations. Therefore, these excited rovibrational states populated at energies above 4 eV are more likely to dissociate in the ground electronic state through pathways (6) and (7) since, for these pathways, the ground state asymptote is below 4 eV (see Fig. 2) or slightly above 4 eV [see Fig. 3(a)]. This dissociation process should be much faster than the tunneling mechanism. Excitation of the third excited state at energies around 7.5 eV (165 nm) or somewhat higher would allow it to overcome the exit barriers of the ground and the first three excited states [see Fig. 4(a)], leading to a fast direct dissociation. In this case, pathway (8) could compete with pathways (6) and (7), but the wavelengths required are expected only in the higher atmosphere. Therefore, upon excitation

of the first excited states and after some internal conversion to lower excited states, fragmentation caused by predissociation mediated by the nonadiabatic couplings associated with the avoided crossings, as well as tunneling and a faster dissociation in the ground state, are the expected dynamical mechanisms. For the excitation of the three first excited states at energies around 7.5 eV, a fast direct dissociation mechanism is also possible.

It is noted that with the grid of points in the C–H₂ distance used in the calculation of the curves in Fig. 4, it is not possible to obtain very smooth curves for several of the electronic states so as to completely characterize the exit barriers in those cases. As a result, for some states, we did not obtain the maximum height and a smooth shape of the barrier. With the current level of theory used in this work, the present calculations are very demanding and, therefore, the number of C–H₂ distance points has to be necessarily limited, leading to a relatively poor resolution in the characterization of some of the exit barriers. We emphasize, however, that characterizing the barriers with a better resolution (thus finding the correct barrier height) would not change the nature of the photodissociation mechanisms proposed earlier. From the shape of the curves in Fig. 4, pathway (8) differs from the other two pathways. Indeed, with the present resolution, the current curves of Fig. 4 already display the relevant information that remarkably higher exit barriers are present in all the electronic states for pathway (8) as compared to the curves associated with pathways (6) and (7), leading to much slower dissociation mechanisms for H₂ elimination than in the case of Br and H elimination.

At this point, a few remarks on the active space chosen in the present calculations should be made. For a system like the present one and considering so many electronic states, there is probably no total guarantee that the active space chosen is similarly accurate for all the fragmentation pathways studied. However, there are some objective criteria that can be used to assess whether the choice of active space is accurate enough. Among the main criteria is the quality of calculated energy magnitudes like vertical excitation energies in the Franck–Condon region and in the asymptote of the curves, the energies of the molecular fragment states (like those of CH₂ and HCB_r), and the spin–orbit splitting of the Br fragment. If the above energy magnitudes compare well to experimental and previously calculated values, then the choice of the active space is expected to be sufficiently accurate. In this sense, our vertical excitation energies for the three first excited states agree very well with the peaks of the three first absorption bands measured experimentally, as discussed at the end of Sec. III A, and also with the energies calculated in Ref. 6 (see Table II). We also checked that the energies of the CH₂ fragments (the asymptotes of the curves in Fig. 2) agree well with the experimental ones, and this is why we could easily assign the products corresponding to these asymptotes. Similarly, the asymptotic energies associated with the HCB_r fragment agree very well with those previously calculated in Ref. 34, as discussed in the supplementary material. Finally, our calculated spin–orbit splitting for Br compares very well with the experimental value (see Table I). All the above results assess the quality of the active space chosen in the current calculations.

It is now interesting to discuss whether solar irradiation and solar actinic fluxes at the required wavelengths are significant enough in the stratosphere and troposphere to cause photodissociation of CH₂Br. Solar actinic fluxes were calculated at different

altitudes in the atmosphere in the range of 120–370 nm.^{35,36} Significant actinic fluxes in the range 285–370 nm were found at 0 km (lower troposphere) and 20 km (middle stratosphere). Important actinic fluxes were also found in the range 170–370 nm at 40 km (upper stratosphere), and a window of somewhat lower fluxes was found at ~200 nm at 20 km (middle stratosphere). The above-mentioned results mean that taking into account the PECs of Figs. 2–4 and the VEEs of Table II, the three first excited states of CH₂Br could be excited in the upper stratosphere, and the first excited state could also be excited in the middle stratosphere and even in the lower troposphere. Moreover, the fourth (excitation at about 216 nm) and fifth (excitation at about 203 nm) excited states could also absorb in the upper and middle stratospheres. The implication is that the Br fragment produced upon photodissociation of CH₂Br may contribute to ozone depletion both in the troposphere and stratosphere.

While the solar actinic fluxes appear to make possible photolysis of CH₂Br in the atmosphere in different excited electronic states, a key question now is whether the CH₂Br radical survives in the atmosphere for enough time to undergo such photolysis. Indeed, CH₂Br can be destroyed by means of reactive collisions with different atmospheric species, mainly O₂. Therefore, in order to elucidate the above point, we need to estimate and compare both the CH₂Br atmospheric photolysis lifetime and the lifetime of CH₂Br loss through competing reactive processes. These lifetimes are obtained with the aid of the present *ab initio* PECs combined with the application of radiation and atmospheric models.

To estimate the above-mentioned two types of CH₂Br lifetimes, we need the CH₂Br absorption cross sections in a range of wavelengths on the one side and the reaction rate constants of CH₂Br with atmospheric species on the other side. The CH₂Br absorption cross sections have been measured in the range of 220–350 nm.^{24,25} As mentioned in the Introduction, the reaction rate constants of CH₂Br + O₂ + (He) have been measured at different atmospheric temperatures in the range 220–450 K.²³ For simplicity, we will restrict the reactive loss of CH₂Br only to reactions with O₂.

From the PECs of Figs. 2–4, it is found that for excitations up to 5 eV (250 nm), only pathway (6) is open for CH₂Br photolysis. In pathway (6), both the first and second excited states can be reached for excitations below 5 eV. On the contrary, for pathway (7), the first excited state displays an exit barrier around 5 eV, so CH₂Br photolysis in this case is expected to be closed or rather slow below 5 eV. A similar behavior is found for pathway (8) due to the high exit barriers of the first excited states. Therefore, if we restrict ourselves to excitation energies up to 5 eV, only pathway (6) will be open, and the quantum yield of the CH₂ + Br products can be considered 1. Now, in order to estimate the CH₂Br atmospheric photolysis lifetime, we will consider the location 40° North, 0° East, and two different altitudes, namely above sea level (troposphere) and 15 km altitude (stratosphere; in this location, the tropopause altitude is approximately 12 km). The time considered was 30 June 2015 at 12:00. The actinic flux is calculated above sea level and at 15 km altitude by integrating the experimental CH₂Br absorption cross sections in the region 280–350 nm using a global climate model (www.acom.ucar.edu/Models/TUV/Interactive_TUV).²⁸ The 280–350 nm range ensures both that at least the first excited state of pathway (6) can be reached and that photons with a

wavelength >290 nm can reach the above sea level region of the troposphere. The CH₂Br atmospheric photolysis rates and lifetimes obtained in this way are 0.010 28 s⁻¹ and 97.28 s, respectively, for the location above sea level and 0.011 51 s⁻¹ and 86.88 s, respectively, for the location at 15 km altitude.

Regarding the CH₂Br + O₂ + (He) reaction, the measured rate constant²³ is $k = (1.2 \pm 0.2) \times 10^{-30} (T/300 \text{ K})^{-4.8 \pm 0.3} \text{ cm}^6 \text{ s}^{-1}$. Assuming [CH₂Br] = 0.65 pptv ($1.6 \times 10^7 \text{ molec cm}^{-3}$) from photolysis of CH₂Br₂ (0.5 pptv) and CH₂BrCl (0.15 pptv) and [O₂] = $5.3 \times 10^{18} \text{ molec cm}^{-3}$, the loss rate and lifetime of CH₂Br for the reaction with O₂ are $1.05 \times 10^{-4} \text{ s}^{-1}$ and 9516.5 s, respectively. Therefore, the CH₂Br reactive loss lifetime is about two orders of magnitude longer than the CH₂Br atmospheric photolysis lifetimes estimated in the troposphere and in the stratosphere. This implies that CH₂Br lives long enough in the atmosphere to photolyze to give at least the CH₂ + Br products.

As discussed earlier, the actinic fluxes in the troposphere and in the stratosphere would allow to excite in principle the first five CH₂Br excited states, where production of the HCBBr fragment is very likely, comparable to the probability of the dissociation pathway (6). The above-mentioned combination of mechanisms is expected to produce dissociation of CH₂Br on several electronic PECs and, therefore, generate HCBBr fragments in different electronic states, including the ground and some excited ones. The MRCI calculations of Burrill and Grein³⁴ on the HCBBr PECs have shown that in the photon energy range accessible in the troposphere and in the stratosphere (up to 6 eV), there are several excited states of HCBBr (up to 10) that can be populated from the ground state (as well as from the first excited states), some of them being repulsive states. Similarly, as for HCBBr, Burrill and Grein³⁷ performed MRCI calculations of the CBr PECs, and they found several dissociative excited states accessible from the ground state (with nonzero oscillator strengths) up to the energy of 6 eV (excitation at 207 nm). This means that after producing the HCBBr and CBr fragments through pathways (7) and (8), they could further dissociate into CH + Br and C + Br fragments, respectively, contributing an additional population of Br atoms to that generated by pathway (6), which will also deplete the ozone population in the atmosphere. It should also be considered the possibility that before absorbing a photon, the HCBBr and CBr fragments could not survive due to collisions and reactions with other molecules abundant in the troposphere and in the stratosphere, like O₂, N₂, and O₃ itself. This type of atmospheric chemistry of HCBBr and CBr is currently unknown, and it would be interesting to investigate and consider in atmospheric models related to ozone depletion.

The shape of the PECs shown in Figs. 2–4 allows us to determine qualitatively how fast the different dissociation mechanisms associated with each fragmentation pathway will occur and, therefore, how the competition between them is expected to be. The first excited PECs associated with pathway (6) are essentially repulsive, so a rather simple mechanism of direct and fast dissociation in the femtosecond time scale is predicted. The PECs of pathway (7) exhibit moderately high exit barriers and avoided crossings. The mechanisms discussed earlier associated with these PECs of internal conversion, predissociation, and tunneling through the barriers involve significantly longer time scales for CH₂Br fragmentation than for pathway (6). An exception to these mechanisms in

pathway (7) would be the PEC of the first excited state, which has a very shallow well and is expected to behave in practice as a repulsive PEC, then leading to a direct and fast dissociation similar to pathway (6). For pathway (8), deeper wells and significantly higher barriers are found in the PECs. This implies similar mechanisms of internal conversion, predissociation, and tunneling as in pathway (7), but involving substantially slower time scales for pathway (8). Even if a rovibrationally excited ground state is reached by internal conversion and dissociation without tunneling can occur in the ground state through pathways (6) and (7), the dissociation time scale will increase remarkably due to the previous slow internal conversion process. Therefore, CH_2Br fragmentation in the atmosphere is expected to proceed dominantly through the fast dissociation mechanisms associated with pathways (6) and (7), producing $\text{CH}_2 + \text{Br}$ and $\text{HCB}r + \text{H}$, respectively. The generally much slower mechanisms of pathway (8) can hardly compete with those of pathways (6) and (7), and then the production of $\text{CBr} + \text{H}_2$ is predicted to be a rather minor dissociation channel unless higher energy photons (around 165 nm) are involved, for which pathway (8) may eventually compete with pathways (6) and (7).

IV. CONCLUSIONS

Photodissociation of the CH_2Br radical is investigated by means of high-level multireference configuration interaction *ab initio* calculations, including spin-orbit effects. All the possible fragmentation pathways of the radical, namely $\text{CH}_2\text{Br} + h\nu \rightarrow \text{CH}_2 + \text{Br}$, $\text{HCB}r + \text{H}$, and $\text{CBr} + \text{H}_2$, are analyzed. Potential-energy curves associated with the ground and several excited electronic states along the dissociating bond distance corresponding to each pathway are obtained. To the best of our knowledge, this is the first time that all the photodissociation pathways of this radical are studied and that spin-orbit effects are considered.

Taking into account the actinic fluxes of solar irradiation in the troposphere and in the stratosphere in the frequency region where the excited potential-energy curves obtained can be accessed from the ground state, it is found that the first five excited electronic states can be populated in those atmospheric regions. The CH_2Br atmospheric photolysis lifetime in the troposphere and in the stratosphere, as well as the CH_2Br loss lifetime through reaction with O_2 , are estimated with the aid of the calculated potential curves combined with the application of radiation and atmospheric models. The CH_2Br loss lifetime is found to be about two orders of magnitude longer than the photolysis lifetimes, which means that CH_2Br survives long enough in the atmosphere to make possible its photolysis.

By analyzing the shape of the calculated potential-energy curves, the possible photofragmentation dynamics mechanisms are discussed. Fragmentation of CH_2Br into $\text{CH}_2 + \text{Br}$ proceeds through a fast direct dissociation mechanism in all the excited states, which are essentially repulsive. The same mechanism holds for dissociation into $\text{HCB}r + \text{H}$ in the first excited state. For the second and higher excited states of this latter pathway, as well as for all the excited states of the pathway leading to $\text{CBr} + \text{H}_2$, the appearance of avoided crossings between states and high exit barriers leads to remarkably slower dissociation mechanisms involving internal conversion between excited states combined with predissociation and dissociation by tunneling through the barriers. Therefore, the pathways

producing $\text{CH}_2 + \text{Br}$ and $\text{HCB}r + \text{H}$ (in the first excited state) by means of faster mechanisms are expected to be the dominant ones, while the much slower pathway producing $\text{CBr} + \text{H}_2$ is predicted to be unlikely. The actinic fluxes of irradiation in the troposphere and in the stratosphere also allow for further excitation of $\text{HCB}r$ and CBr to repulsive excited states that would lead to dissociation into $\text{CH} + \text{Br}$ and $\text{C} + \text{Br}$ products, respectively, that would additionally contribute to ozone depletion. Another likely possibility is that the $\text{HCB}r$ and CBr fragments may collide and react with other abundant reagents in the atmosphere (mainly O_2). In this sense, it would be interesting to investigate the unknown chemistry of these fragments with O_2 and other molecules present in the atmosphere in order to include them in atmospheric models.

SUPPLEMENTARY MATERIAL

The supplementary material contains additional results, descriptions, and discussions related to the methodology applied and some of the potential-energy curves calculated.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

F. Charfeddine: Formal analysis (equal); Investigation (equal); Visualization (equal). **A. Zanchet:** Conceptualization (lead); Supervision (lead); Validation (equal); Writing – review & editing (equal). **O. Yazidi:** Conceptualization (equal); Writing – review & editing (equal). **C. A. Cuevas:** Conceptualization (equal); Formal analysis (equal); Writing – original draft (equal). **A. Saiz-Lopez:** Conceptualization (equal); Funding acquisition (lead); Writing – review & editing (equal). **L. Bañares:** Conceptualization (equal); Funding acquisition (equal); Writing – review & editing (equal). **A. García-Vela:** Conceptualization (equal); Funding acquisition (equal); Supervision (equal); Validation (equal); Writing – original draft (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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