

First principles study of the OH radical: $B^2\Sigma^+ - X^2\Pi$ and $D^2\Sigma^- - X^2\Pi$ rovibronic transitions

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(Received 19 January 2024; accepted 21 October 2025; published 22 January 2026)

OH radical can be found in comets, stellar atmospheres, planetary atmospheres, interstellar clouds, exoplanets, the solar photosphere, and sunspots, making it a significant astrophysical molecule. Its detection relies on its emission properties, intrinsic to the molecules' rovibrational levels. This work presents high-level *ab initio* calculations of the electronic structure of OH radical using complete active space self consistent field/multiReference configuration interaction calculations, including Davidson correction methods with large basis sets and extensive treatment of the electron correlation. The adiabatic potential energy curves of the low-lying doublet and quartet electronic states of the hydroxyl, in the representation $^{2S+1}\Lambda^{+/-}$, are investigated. Additionally, a systematic investigation of the transition dipole moment function (TDMF) for the $B^2\Sigma^+ - X^2\Pi$ and $D^2\Sigma^- - X^2\Pi$ transitions has been done along with the Franck-Condon factors of these systems. The computed TDMF and potential energy function are used in Le Roy's LEVEL and Western's PGOPHER programs, in combination with experimental literature line positions, to calculate rovibronic $B^2\Sigma^+ - X^2\Pi$ and $D^2\Sigma^- - X^2\Pi$ transitions. The corresponding "first principles"-based line lists include line intensities, line positions with the relevant quantum numbers of the upper and lower states, e/f parity, and Einstein A coefficients. The results show good agreement with previously published experimental and theoretical data, including a corresponding updated MARVEL (measured active rotational-vibrational energy levels) analysis of the lowest excited states of the OH molecule.

DOI: [10.1103/h853-qnjt](https://doi.org/10.1103/h853-qnjt)

I. INTRODUCTION

The hydroxyl radical (OH) is a crucial component of cometary gases, diffuse, dense, and shocked areas of interstellar gas, combustion gases, and the pure and polluted terrestrial atmosphere [1,2]. It exhibits a wide range of thermochemical properties and plays a vital role in several chemical, combustion, astronomical, and atmospheric environments [3]. It is considered the most significant free radical in the Earth's atmosphere as it effectively removes accumulated organic molecules from the troposphere, preventing their rapid accumulation and potential harm to human beings [4]. Moreover, OH molecules can be produced in the Martian atmosphere by the photodissociation of water vapor and in several chemical reactions, such as those involving thermal molecular hydrogen and energetic oxygen atoms $O + H_2 \rightarrow H + OH$ [5,6]. Emission and absorption spectra of OH radicals within the Martian atmosphere can lead to a better understanding of these processes. For example, they can help monitor the variation of

its abundance with altitude. Astronomical spectra of OH radicals can be better interpreted through a detailed identification of their line list. These line lists offer a valuable diagnostic of the environments in which OH is present.

The rovibronic spectra of OH have been thoroughly explored using various high-resolution molecular spectroscopy techniques. A significant number of OH transitions have been studied, especially the OH Meinel bands ($X^2\Pi - X^2\Pi$ transition) [7–10] and $A^2\Sigma^+ - X^2\Pi$ transition [2,11–17]. The $A^2\Sigma^+ - X^2\Pi$ transition line list recently produced by Yousefi, *et al.* [2] has proven its effectiveness in analyzing the solar and stellar (HD196944) spectra, confirming its high accuracy. Below, we only highlight a few critical works related to our interest in $B^2\Sigma^+ - X^2\Pi$ and $D^2\Sigma^- - X^2\Pi$ bands. A complete literature on OH for the $B^2\Sigma^+ - X^2\Pi$ and $D^2\Sigma^- - X^2\Pi$ transitions can be found in Hwang, *et al.* [18] and Heays, *et al.* [19], respectively. Langhoff, *et al.* [1] initially calculated transition probabilities for the $B^2\Sigma^+ - X^2\Pi$ in 1982. They also estimated the radiative lifetimes of the $B^2\Sigma^+$, $v' = 0$, and $v' = 1$ vibrational levels to vary between 235–350 and 410–590 ns, respectively. Sappay and Copeland [20] reported the line positions for the $B^2\Sigma^+ - X^2\Pi$ (0, 12) and the Meinel bands (12, 8) using a two-laser double resonance method. Coxon, *et al.* [21] examined the $X^2\Pi - X^2\Pi$, $A^2\Sigma^+ - X^2\Pi$, $B^2\Sigma^+ - X^2\Pi$, $C^2\Sigma^+ - A^2\Sigma^+$, and $B^2\Sigma^+ - A^2\Sigma^+$ systems using laser-induced fluorescence (LIF) [20,22] to derive different molecular constants for the $X^2\Pi$ ($v = 8, 12$), $A^2\Sigma^+$

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($v = 4-9$), $B^2\Sigma^+$ ($v = 0, 1$), and $C^2\Sigma^+$ ($v = 0, 1$) vibrational levels. Later on, Copeland, *et al.* [23] measured the line positions of the (0, 7), (0, 8), (0, 9), (0, 11), (0, 13), and (1, 9) vibrational bands of the $B^2\Sigma^+ - X^2\Pi$ transitions using LIF and extracted the molecular constants for $X^2\Pi$ ($v = 7-9, 11-13$) and $B^2\Sigma^+$ ($v = 0, 1$). Hwang, *et al.* [18] obtained rovibrational spectra of the $B^2\Sigma^+ - X^2\Pi$ band using LIF and measured the OH ($B, v' = 0$) collision-free lifetimes. The molecular constants for the $X^2\Pi$ ($v = 0-13$) and $B^2\Sigma^+$ ($v = 0, 1$) states of OH were updated by Bernath and Colin [24] in 2009, using previously published laboratory data and lines [25] acquired from infrared sun spectra collected by the ACE (Atmospheric Chemistry Experiment [26]) satellite. Later on, *ab initio* potential energy curves (PECs) for the ground and low-lying excited electronic states of OH have been computed by Qin and Zhang [27] and Vamhindi and Nsangou [28]. Furtenbacher, *et al.* [3] recently gathered and analyzed using MARVEL (measured active rotational-vibrational energy levels) all available experimental rovibronic data from the literature for transitions among $X^2\Pi$, $A^2\Sigma^+$, $B^2\Sigma^+$, and $C^2\Sigma^+$ states. The spectroscopic network (SN)-based method helped determine energy levels for the four doublet electronic states with reliable, statistically significant individual uncertainties.

The $D^2\Sigma^-$ state of OH was first discovered by Douglas [29] in 1974. They recorded the first absorption spectra of OH and OD radicals for the $D^2\Sigma^- (v' = 0) \leftarrow X^2\Pi (v'' = 0)$ band near the 1200 Å region photographically. A set of molecular constants was generated for the lowest $D^2\Sigma^-$ state of OH and $X^2\Pi$, $A^2\Sigma^+$, and $D^2\Sigma^-$ states of OD. In the 1980s, Langhoff, *et al.* [1] and Van Dishoeck, *et al.* [30,31] have done a series of theoretical studies to determine the photoabsorption and dissociation properties of $D^2\Sigma^-$ ($v = 0$ and $v = 1$ levels) and other excited states of the OH radical. Moreover, between 1990 and 2005, several laser-based resonance-enhanced multiphoton ionization experiments, such as those done by Collard, *et al.* [32], Beer, *et al.* [33], McRaven, *et al.* [34], and Greenslade [35], have recorded high-spectral-resolution absorption spectra for the $D^2\Sigma^- (v' = 0) \leftarrow X^2\Pi (v'' = 0)$ and other states of OH. Recently, Heays, *et al.* [19] detected VUV photoabsorption spectra for the $D^2\Sigma^- (v' = 0) \leftarrow X^2\Pi (v'' = 0)$, $D^2\Sigma^- (v' = 1) \leftarrow X^2\Pi (v'' = 0)$, and $A^2\Sigma^+ (v' = 0) \leftarrow X^2\Pi (v'' = 0)$ bands of OH and OD molecules, and deduced the lifetime of the $D^2\Sigma^-$ state for the $v' = 0$ and $v' = 1$ levels.

To summarize, to our knowledge, theoretical and experimental studies have been done to investigate the vibrational $B^2\Sigma^+ - X^2\Pi$ transition of OH [1,18,20-24,36], but there have been no rovibrational investigations in this area. Similarly, experimental studies in the literature have addressed the vibrational $D^2\Sigma^- (v' = 0, 1) - X^2\Pi (v'' = 0)$ transition [15,19,29,31-37] without highlighting its rovibrational aspects. In this work, we present comprehensive “first principles”-based investigations of the rovibrational $B^2\Sigma^+ (v' = 0-1) - X^2\Pi (v'' = 0-13)$ and $D^2\Sigma^- (v' = 0-1) - X^2\Pi (v'' = 0-13)$ OH transition. The calculations rely on an investigation of the adiabatic PECs and the transition dipole moment curves (TDMCs) of the low-lying doublet electronic states of OH, using *ab initio* complete active space self consistent field (CASSCF)/multireference

configuration interaction calculations, including Davidson correction (MRCI + Q) methods with a large basis. The corresponding spectroscopic parameters have been determined. Additionally, we present an updated MARVEL analysis comprising the $D^2\Sigma^-$ state and compare it with our results to better evaluate their accuracy. To the best of our knowledge, this is the first theoretically investigated rovibrational line list for the $B^2\Sigma^+ - X^2\Pi$ and $D^2\Sigma^- - X^2\Pi$ systems. This study offers additional insights into molecular structure and spectroscopic analysis of a wide range of vibrational and rotational levels of OH. These play a crucial role in analyzing the emission and absorption spectra of the radical, as they enable researchers to identify and characterize its corresponding lines. Such data help in understanding the OH radical's behavior in different environments and for various applications, including astronomical [38-40], combustion [41-43], and atmospheric [44,45] studies.

This paper is organized as follows: Sec. II presents the computational methods used for the *ab initio* calculations, the generation of the line lists, and the MARVEL method. Section III displays the results and corresponding discussions.

II. COMPUTATIONAL DETAILS

A. *Ab initio* calculation

The *ab initio* study of the low-lying electronic states of OH radical has been theoretically conducted using molpro computing package [46]. Corresponding PEC of $X^2\Pi$, $A^2\Sigma^+$, $B^2\Sigma^+$, $1^2\Sigma^-$, $D^2\Sigma^-$, $C^2\Sigma^+$, $2^2\Pi$, $1^2\Delta$, $2^2\Delta$, $1^4\Pi$, $1^4\Sigma^-$, $2^4\Sigma^-$, $3^4\Sigma^-$, and $4^4\Sigma^-$ states and transition dipole moment functions (TDMFs) of the $B^2\Sigma^+ - X^2\Pi$ and $D^2\Sigma^- - X^2\Pi$ transitions were calculated. The study was performed using the CASSCF method, followed by the MRCI calculations, including Davidson correction [47]. Both the oxygen and hydrogen atoms were treated in an all-electron scheme using the large Dunning's augmented correlation-consistent polarized valence septuple- ζ (aug-cc-pV7Z) basis set, including *spdfghi* functions [48] for the PEC and TDMF of the $B^2\Sigma^+ - X^2\Pi$ and $D^2\Sigma^- - X^2\Pi$ transitions. The active space includes 7σ (O: $2s, 2p_0, 3s, 3p_0$; H: $1s, 2s, 2p_0$) and 3π (O: $2p_{\pm 1}, 3p_{\pm 1}$; H: $2p_{\pm 1}$) molecular orbitals, where all the calculations of the active space are done in the C_{2v} subgroup of the $C_{2\infty}$ symmetry. The active orbitals are distributed into the irreducible representation as $7a_1, 3b_1, 3b_2, 0a_2$, denoted by [7, 3, 3, 0].

The spectroscopic characterization of the PECs is done as in previous work [49-52] i.e., T_e , R_e , ω_e , $\omega_e x_e$, B_e , and α_e of the bound states are obtained by fitting the energy data near the equilibrium position to a Dunham polynomial as a function of the internuclear distance. The polynomial degrees are selected based on the statistical errors of the coefficients. The dissociation energy (D_e) of a state is calculated by subtracting the energy at a large internuclear distance (where dissociation occurs) from its equilibrium electronic energy.

B. Molecular constants

Accurate and precise molecular constants are critical in describing the rovibrational levels in a given electronic state

of a diatomic molecule. Previous studies have been done to compute the molecular constants for the low vibrational levels ($v = 0, 1$) of the $B^2\Sigma^+$ state of OH, such as Coxon, *et al.* [21] and Copeland, *et al.* [23]. Bernath, *et al.* [24] extended the analysis to higher vibrational levels, reaching up to $v = 4$. We used the molecular constants obtained by Bernath, *et al.* [24] for the $B^2\Sigma^+$ and $X^2\Pi$ states, who provided improved molecular constants through the analysis of previously published laboratory data [8,53,54] together with lines gathered from orbit-based infrared solar spectra recorded by atmospheric trace molecule spectroscopy [54].

The energy of the lowest lying rovibrational level of the $D^2\Sigma^-$ ($v = 0$) state of the OH molecule is reported in the literature as $81\,797.95\text{ cm}^{-1}$, $81\,795.8\text{ cm}^{-1}$, and $81\,798.3457\text{ cm}^{-1}$, relative to the lowest rovibrational energy level $X^2\Pi$ ($v = 0$) F_{1e} ($J = 3/2$) (where F_1 represents the spin component and e is the parity) as stated by Douglas [29], Collard, *et al.* [32], and Heays, *et al.* [19]. A study by Beer, *et al.* [33] valued the energy to be $81\,815.8\text{ cm}^{-1}$, and stated in the text to have a good agreement with Douglas' results. This may indicate that Beer, *et al.* [33] have used a different zero-point energy. In Western's PGOPHER program [55], the lowest nonrotational vibrational level ($v = 0$) is considered the zero-point energy for the corresponding molecular constants. Considering the shift described above, we use the laboratory molecular constants corresponding to $v = 0$ and $v = 1$ of the $D^2\Sigma^-$ state adjusted to the high-resolution experimental spectra in the recent study of Heays, *et al.* [19], relative to the ground state $X^2\Pi$ ($v = 0$). The resulting values are as follows: $T(D^2\Sigma^-, v = 0) = 81\,778.576\,98\text{ cm}^{-1}$ and $T(D^2\Sigma^-, v = 1) = 84\,341.739\,85\text{ cm}^{-1}$.

C. Transition dipole moment matrix element transformation

The computed TDMF and PEC were input to Le Roy's LEVEL program [56]. The TDMF and PEC were interpolated using cubic splines with a radial range of integration of $0.50\text{--}3.50\text{ \AA}$ and a radial step size of $0.0006\text{ \AA}$. LEVEL program produces vibrational wavefunctions of given electronic states by solving the one-dimensional Schrödinger equation using the procedure of Numerov-Cooley [56]. These wavefunctions are then used to compute the transition dipole moment matrix elements (TDMMEs) of the given transitions. LEVEL16 program does not account for electron spin, corresponding to Hund's case (b) basis. These matrix elements are expressed in the form

$$\langle v' \Lambda' N' | T_q^k | v'' \Lambda'' N'' \rangle, \quad (1)$$

where T_q^k represents the dipole moment operator expressed in the spherical tensor form, q is 0 for parallel and ± 1 for perpendicular transitions, and k is the transition rank equal to 1 for single photon electric dipole transition. v'' and v' , Λ'' and Λ' , and N'' and N' represent the upper and lower vibrational levels quantum numbers, those associated with the projection of the total orbital angular momentum on the internuclear axis, and the angular momentum excluding the spin of the upper and lower states, respectively.

The PGOPHER program [55] uses Hund's case (a) basis set, where the orbital angular momentum and spin are strongly coupled with the internuclear axis. Therefore, to use the

calculated TDMMEs for intensity calculations in PGOPHER, it is required to convert these matrices from Hund's case (b) to Hund's case (a) basis set, which includes electron spin (J). This was done following Brooke, *et al.*'s method [10] through the following equation:

$$\begin{aligned} & \langle \eta' \Lambda' | T_q^k(J' \Omega' J \Omega) | \eta \Lambda \rangle \\ & \geq (-1)^{J'-\Omega'} \begin{pmatrix} J' & k & J \\ \Omega' & q & \Omega \end{pmatrix}^{-1} \sum_{N, N'} (-1)^{N-N'+S+J+k+\Lambda} \\ & \times (2N'+1)(2N+1) \begin{pmatrix} J' & S & N' \\ \Omega' & -\Sigma & -\Lambda' \end{pmatrix} \\ & \times \begin{pmatrix} J & S & N \\ \Omega & -\Sigma & -\Lambda \end{pmatrix} \begin{Bmatrix} N' & J' & S \\ J & N & k \end{Bmatrix} \\ & \times \begin{pmatrix} N' & k & N \\ -\Lambda' & q & \Lambda \end{pmatrix} \langle \eta' \Lambda' | T_q^k(N' N) | \eta \Lambda \rangle. \quad (2) \end{aligned}$$

The transformation is expressed using Wigner 3- j and 6- j symbols, where $\langle \eta' \Lambda' | T_q^k(J' \Omega' J \Omega) | \eta \Lambda \rangle$ are the matrix elements in Hund's case (a) and $\langle \eta' \Lambda' | T_q^k(N' N) | \eta \Lambda \rangle$ are the matrix elements in Hund's case (b). Σ and Ω represent the spin and total angular momentum projections on the internuclear axis, respectively. S is the rovibronic symmetry, and η' and η represent the vibrational quantum number and electronic state of the upper and lower states, respectively.

D. Line list calculations

The transformed dipole moment matrix elements in Hund's case (a) basis were imported into PGOPHER [55] to produce a line list with line intensities, considering vibrational and rotational dependence. The Supplemental Material [57] contains extensive line lists for the electronic transitions $B^2\Sigma^+ - X^2\Pi$ and $D^2\Sigma^- - X^2\Pi$ of the OH radical, which include line positions with relevant quantum numbers of the upper and lower states, e/f parity, line intensities, rotational line strength, and Einstein A coefficients.

PGOPHER calculates Einstein A coefficients $A_{\eta' J' \rightarrow \eta J}$ (given in s^{-1}) using the equation

$$\begin{aligned} A_{\eta' J' \rightarrow \eta J} &= \frac{16\pi^3 v^3}{3\epsilon_0 h c^3} \frac{S_{\eta' J' \rightarrow \eta J}}{(2J' + 1)} \\ &= 3.136\,188\,94 \times 10^{-7} \frac{v^3 S_{\eta' J' \rightarrow \eta J}}{(2J' + 1)}, \quad (3) \end{aligned}$$

where $S_{\eta' J' \rightarrow \eta J}$ is the line strength (in Debye squared) and v is the wave number (in cm^{-1}).

III. RESULTS AND DISCUSSION

A. Potential energy curves and spectroscopic constants

The PECs of the ground $X^2\Pi$ and low-lying doublet and quartet electronic states of OH molecule as a function of the internuclear separation R are calculated over the range $0.50\text{ \AA} \leq R \leq 5.00\text{ \AA}$, with increments of $0.02\text{ \AA}$. The resulting curves are shown in Fig. 1 in comparison with the PECs from Langhoff, *et al.* [1] and the Rydberg-Klein-Rees (RKR) PECs of Yousefi, *et al.* [2]. Our PECs are found to be in very good agreement with the RKR potential energies of $X^2\Pi$ and

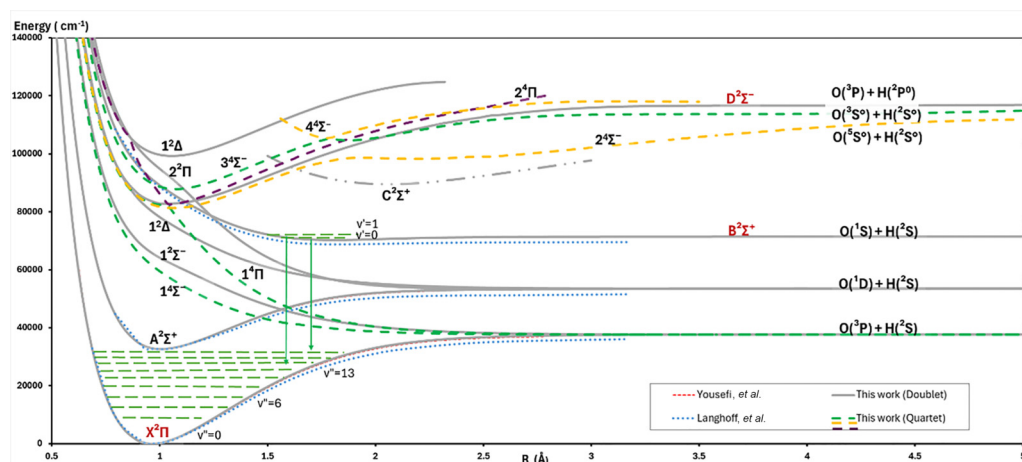


FIG. 1. PECs calculated in this work compared with Langhoff, *et al.* [1] (dotted blue) and RKR PECs by Yousefi *et al.* (dashed red) [2]. The vibrational levels added in green are for graphical representation and are not accurately located.

$A^2\Sigma^+$ of Yousefi, *et al.* [2]. However, Langhoff's curves seem to be systematically shifted to lower asymptotic limits, even though their equilibrium points and well shapes agree well with our and Yousefi's RKR curves. The perfect accordance between our curves and the RKR ones points, however, to better confidence in our results compared to the ones obtained by Langhoff, *et al.*

Based on this study, the bound $2^4\Sigma^-$ and $4^4\Sigma^-$ states are in the vicinity of the $D^2\Sigma^-$ state, causing a crossing between the rotational series of the three states, which may represent the local perturbation of spin-orbit interaction mentioned by Heays, *et al.* [19]. This perturbation results in the shifting of certain levels of the OH D ($v = 0$) due to a weak interaction with neighboring states in its vicinity.

The investigated doublet and quartet electronic states of OH radical correlate at large internuclear distances to the $[\text{O}(2s^2 2p^4, {}^3\text{P}) + \text{H}(1s^1, {}^2\text{S})]$, $[\text{O}(2s^2 2p^4, {}^1\text{D}) + \text{H}(1s^1, {}^2\text{S})]$, $[\text{O}(2s^2 2p^4, {}^1\text{S}) + \text{H}(1s^1, {}^2\text{S})]$, $[\text{O}(2s^2 2p^3({}^4\text{S}^\circ)3s, {}^5\text{S}^\circ) + \text{H}(2s^1, {}^2\text{S})]$, $[\text{O}(2s^2 2p^3({}^4\text{S}^\circ)3s, {}^3\text{S}^\circ) + \text{H}(2s^1, {}^2\text{S})]$, and $[\text{O}(2s^2 2p^4, {}^3\text{P}) + \text{H}(2p, {}^2\text{P}^\circ)]$ dissociation limits. Table I shows the dissociation limit energies and corresponding relative errors between our theoretical values and the experimental ones by Kramida, *et al.* [58] from the NIST atomic spectra database. The comparison shows a minimal difference of less than 0.6% at all dissociation limits.

It is worth noting that, contrary to full CI methods, the MRCI method is neither size-consistent nor size-extensive

[59]. The usage of the Davidson correction in this work aimed to correct the lack of size extensivity in the adopted method. At the same time, some studies presented comparisons about the effect of different correction methods at the dissociation limits. In particular, a recent study has shown that in some cases, the implementation of the Davidson correction can lead to an improvement of the Bond Dissociation Energy value [60]. However, other investigations proposed to use alternative correction methods that would better represent the molecular behavior of molecules when the constituting atoms are far apart, including the Pople correction [61]. Accordingly, the authors performed additional calculations to better understand and validate the behavior of the OH molecule at the dissociation limit, including the use of the MRCI method (with no correction), MRCI with Pople correction, and MRCI with Davidson correction, and made comparisons on the value of the dissociation energy with similar previous work [37,62]. In all cases, the MRCI + Q method followed in this work gave the closest results and the least relative error with respect to the dissociation energy of the separated atoms, at a large internuclear distance.

The resulting spectroscopic constants are given in Table II. The comparison of our calculated value of R_e for the ground and the investigated low-lying excited states with those given in the literature shows very good agreement, with relative differences smaller than 3.80%. Similarly, the remaining spectroscopic parameters have average percentage errors

TABLE I. The lowest dissociation limit of the lowest doublet states of OH radical.

Dissociation to atomic levels O + H	Dissociation energy limit of OH levels, this work (cm ⁻¹)	Molecular states of OH	Total dissociation energy limit of O + H atoms [58] (cm ⁻¹)	Relative error (%)
O(2s ² 2p ⁴ , ³ P) + H(1s, ² S)	0	X ² Π, 1 ² Σ ⁻ , 1 ⁴ Π, 1 ⁴ Σ ⁻	0	0.00
O(2s ² 2p ⁴ , ¹ D) + H(1s, ² S)	15 856.364	A ² Σ ⁺ , 2 ² Π, 1 ² Δ	15 867.862	0.07
O(2s ² 2p ⁴ , ¹ S) + H(1s, ² S)	33 806.384	B ² Σ ⁺	33 792.583	0.04
O(2s ² 2p ³ (⁴ S ^o)3s, ⁵ S ^o) + H(1s, ² S)	73 492.521	2 ⁴ Σ ⁻	73 768.200	0.37
O(2s ² 2p ³ (⁴ S ^o)3s, ³ S ^o) + H(1s, ² S)	77 239.757	3 ⁴ Σ ⁻	76 794.978	0.58
O(2s ² 2p ⁴ , ³ P) + H(2p, ² P ^o)	82 137.481	D ² Σ ⁻	82 258.919	0.15

TABLE II. Calculated spectroscopic constants of the *ab initio* low-lying doublet bound states of OH at spin-free MRCI+Q level of theory in comparison to experimental and theoretical data reported in the literature.

State	Method	T_e (cm ⁻¹)	ΔT_e (%)	R_e (Å)	ΔR_e (%)	ω_e (cm ⁻¹)	$\Delta \omega_e$ (%)	$\omega_e x_e$ (cm ⁻¹)	$\Delta \omega_e x_e$ (%)	B_e (cm ⁻¹)	ΔB_e (%)	α_e (cm ⁻¹)	D_e (cm ⁻¹)	ΔD_e (%)
X ² Π	This work	0		0.970		3735.418		80.658		18.896		0.727	37 410.347	
	MRCI+Q/V6Z [28]			0.970	0.00	3734.016	0.04	85.708	5.89	18.872	0.13	0.712	37 440.237	0.08
	MRCI/CBS [67]			0.970	0.00	3719.000	0.44	85.830	6.03	18.940	0.23	0.758		
	MCSCF [68]			0.974	0.41	3741.000	0.15	86.800	7.08					
	CI [1]			0.980	1.02	3614.51 ^a	3.24			18.32 ^a	3.05		36 053.000	3.76
	CCSD(T) [69]			0.980	1.02	3739.080	0.10	85.127	5.25	18.870	0.14		37 141.812	0.72
	Exp. [64]			0.970	0.00	3737.761	0.06	84.881	4.98	18.910	0.07	0.724	37 270.861	0.37
A ² Σ ⁺	This work	32 627.42		1.012		3180.554		89.456		17.363		0.839	20 825.745	
	MRCI+Q/V6Z [28]	32 602.00	0.09	1.010	0.20	3178.252	0.07	84.608	5.42	17.262	0.58	0.825	20 881.683	0.27
	MRCI/CBS [67]	33 148.00	1.56	0.960	5.14	3230.000	1.53	101.570	11.93	17.400	0.21			
	MCSCF [68]	33 912.00	3.78	1.021	0.88	3124.000	1.78	101.000	11.43				19 196.000	7.83
	CI [1]			1.010	0.20	2910.94 ^a	8.48			17.96 ^a	3.32		18 470.090	11.31
	Exp. [64]	32 684.10	0.17	1.012	0.00	3178.860		92.917	3.72	17.358	0.03	0.787		
	Exp. [65]						0.05						20 405.816	2.02
B ² Σ ⁺	This work	69 987.75		1.809		898.253		218.709		5.391		0.737	1211.803	
	CI [1]			1.840	1.68	793.080 ^a	11.71						806.55	33.44
	Exp. [64]	69 774.00	0.31	1.869	2.74	660	26.52			5.086	5.66			
D ² Σ ⁻	This work	82 817.62		1.040		2925.203		163.981		15.522		1.159	34 560.985	
	Exp. [29]	82 130.00	0.84	1.081	3.79	2954.00	0.97			15.218	7.89	0.711		

^aCalculated in this work using Langhoff, *et al.*'s [1] PECs.

of 0.93%, 3.30%, 5.33%, 1.24% 7.44%, and 6.57% for T_e , ω_e , $\omega_e x_e$, B_e , α_e , and D_e , respectively.

The values of T_e generally agree with previous experimental and theoretical work for the investigated states. One has to note, however, that in performing *ab initio* calculations, a multitude of factors, such as the basis sets and active spaces used, affect the resulting spectroscopic constants. For example, Langhoff, *et al.* [1] used the configuration interaction (CI) method to calculate the electronic structure and transition properties of the OH molecule. In their work, the authors have shown that the use of two different types of basis sets led to changes in the values of T_e that can reach up to hundreds of wave numbers; in fact, they had obtained for the B²Σ⁺ a T_e value of 68 799 cm⁻¹ with one basis set and 68 235 cm⁻¹ with another.

The T_e value obtained in this work for the B²Σ⁺ state shows agreement with the experimentally obtained value by Barrow, equal to 69 774 cm⁻¹ [63], as portrayed in the Huber and Herzberg's database [65]. The difference of about 200 cm⁻¹ between the two values can be attributed to several factors, one of which, explicitly mentioned by Barrow, is the high uncertainty in the procedure that he followed for the determination of the zero point energy (G_0) of this excited state. This last was used for the determination of T_e , in combination with spectroscopic constants by Herzberg [64]. In fact, the author states that the vibrational levels of the B²Σ⁺ probably depart very considerably from those of a simple harmonic oscillator, and that the best he could assume was following a three-constant expression for the determination of G_0 . He also cites "uncertainties in the values of G_0 " in the same manuscript.

Such uncertainties are also highlighted through the important differences in the values of T_{00} (about 40 cm⁻¹)

mentioned in Ref. [63], and the work published in 1969 by Carlone and Dalby [65]. This difference probably stems from a better accuracy in the experimental setup of the most recent work.

The same experimental uncertainty issue applies to the D²Σ⁻ state, qualified as "uncertain data" according to Huber and Herzberg's [64] notation. Finally, the T_e value obtained in this work for B²Σ⁺ (69 987 cm⁻¹) shows very close agreement with previous work [18,66] following similar MRCI methods, with respective values of 70 048 and 70 069 cm⁻¹.

B. Transition dipole moment function

The precision of the TDMF is essential to obtain accurate line intensities. For this reason, we chose to use the augmented correlation basis sets mentioned in Sec. II A, which contain diffuse and extra polarization functions. Curves obtained in this work for TDMF of B–X transition are presented in Fig. 2. These are compared to those of Langhoff, *et al.* [1], who calculated them following the CI method using different basis sets. Ours agrees closely with set I, consisting of a Slater basis set that incorporates correlation effects in the low-lying valence states but differs slightly from sets II and III, which include a Slater and a Gaussian basis set, respectively, and do not account for the correlation effects [1].

Similarly, the calculated TDMF of D²Σ⁻ – X²Π transition is shown in Fig. 3, with a comparison with those calculated by Dishoeck, *et al.* [31] and Van der Loo, *et al.* [37]. The basis set I used by Dishoeck, *et al.* [31] contains Slater functions without a diffuse function on the oxygen atom (only *s* function on H atom). In contrast, basis sets II and III contain diffuse functions (3*s* and 3*p* to the oxygen atom), with Slater and Gaussian functions, respectively, and basis IA includes

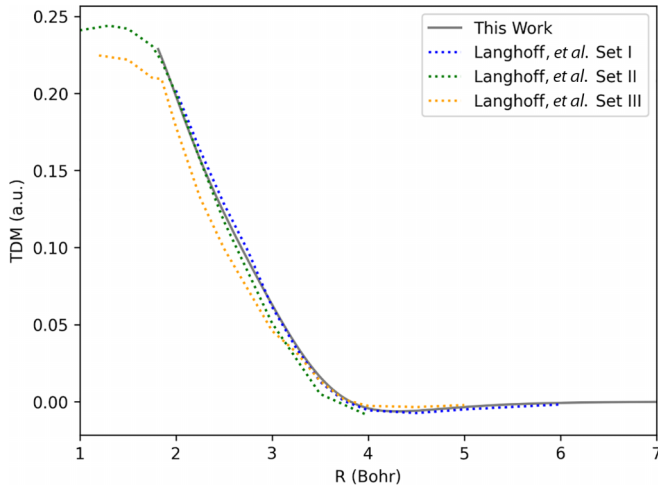


FIG. 2. *Ab initio* transition dipole moment curve of B–X transition of OH compared with Langhoff, *et al.* [1].

diffuse functions to the oxygen atom that are added to the augmented basis set I. In general, our calculated TDMF is closer to Van der Loo, *et al.*'s [37] TDMFs, which are computed using (doubly) augmented correlation-consistent polarized valence 5-zeta with active space including 6σ 1π molecular orbitals.

C. Einstein A coefficient and radiative lifetime

The Einstein A coefficient, as represented in Eq. (3), depends on two significant parameters: ν (wave number) in its cubic form and S (line strength, which represents the square of the TDMMEs [55]), representing the coupling between the potential energy and transition dipole moment curves. The Einstein A coefficients with relevant quantum numbers, including rotational and vibrational dependence, were calculated in this work for all possible bands by summing all possible transitions from $J' = 2.5$ in the F_1 spin component for both the $B^2\Sigma^+ - X^2\Pi$ and $D^2\Sigma^- - X^2\Pi$ transitions of OH. The summation of the Einstein A coefficients $A_{\nu'\nu''}$ at

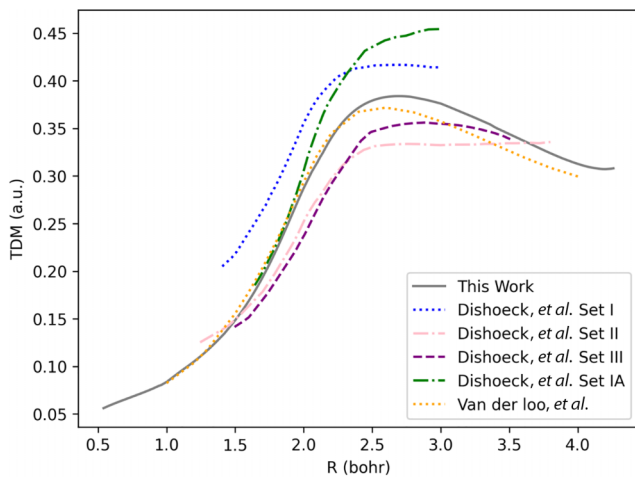


FIG. 3. *Ab initio* transition dipole moment curve of the D–X transition of OH compared with Dishoeck, *et al.* [31] and Van der loo, *et al.* [37].

different rotational levels J' and F_1/F_2 spin component gives approximately similar results.

The $B^2\Sigma^+$ state minimum is at a considerable internuclear distance R , which indicates that the transition probabilities with the ground state will be more significant for higher vibrational levels. Table III compares the B–X transition Einstein A coefficients ($A_{\nu'\nu''}$) for the bands ($\nu' = 0-1$ and $\nu'' = 0-13$) obtained in this work with those reported by Langhoff, *et al.* [1]. The values of Einstein A coefficients exhibit significant differences, around $3.2\% \leq \frac{\Delta A_{\nu'\nu''}}{A_{\nu'\nu''}} \leq 30.9\%$ for the lower vibrational levels, $0 \leq \nu'' \leq 6$, and around $3.3\% \leq \frac{\Delta A_{\nu'\nu''}}{A_{\nu'\nu''}} \leq 97.6\%$ for the higher vibrational levels, $7 \leq \nu'' \leq 13$. This discrepancy arises from differences in both the PEC and TDMF calculated in this work compared to those of Langhoff, as illustrated in Figs. 1 and 2. In fact, the former shows a significantly visible deviation in the PEC. The spectroscopic constants describing Langhoff, *et al.*'s [1] potential energy curves PECs are displayed in Table II. The comparison between our values and Langhoff *et al.*'s for the $B^2\Sigma^+$ state shows an excellent agreement with percentage relative differences of 0.0%, 0.0%, 0.5%, and 0.7% for T_e , R_e , B_e , and D_e , respectively. However, there is a significant divergence in the value of ω_e (% relative difference = 11.71%). Figure 1 agrees with our findings, where the value of ω_e for Langhoff *et al.*'s PEC ($\omega_e = 793.08 \text{ cm}^{-1}$) is smaller than that obtained with the present work ($\omega_e = 898.253 \text{ cm}^{-1}$), reflecting a broader curve in Langhoff *et al.*'s PEC compared with our curve. This discrepancy is probably the leading source of the coupling term (S) difference, resulting in different Einstein A coefficient values at the lower and higher vibrational levels. One has to note, however, that our MRCI PEC is closer to the RKR PEC by Yousefi, *et al.* [2] and that Langhoff, *et al.* [1] reported a relative error of $\pm 20\%$ to account for the range of lifetime across the three different basis sets they used. Given such discrepancy, we also calculated the Einstein A coefficients using our PECs and Langhoff *et al.*'s TDMF basis set I along with Bernath, *et al.*'s [24] molecular constants (Scenario I) for the B–X transition, presented in Table III. A significant decrease in the percentage error was observed, with an average reduction of 70%, indicating that the primary source of the discrepancy is Langhoff *et al.*'s data.

In this analysis, the wave numbers (ν) are computed using the laboratory molecular constants provided by Bernath, *et al.* [24]. At the same time, the TDMMEs are derived by solving the Schrödinger equation for the nuclear motion using the potential energy curves with the transition dipole moment curve. Both the Einstein A coefficients and line strength S show similar trends for the calculations obtained using this work's PECs and TDM, as well as those of Scenario I, as represented in Fig. 4.

For $0 \leq \nu \leq 7$, the Einstein A coefficient values calculated in Scenario I are slightly higher than those in this work because the corresponding line strengths (S) are somewhat larger than ours in this range. As ν increases, the difference between the two S values increases, and they both reach a maximum at $\nu'' = 8$, then decrease until the line strength values (S) are nearly equal around $\nu'' = 12$. The same behavior is reflected for the Einstein A coefficients, suggesting that the TDM plays a crucial role in their determination.

TABLE III. The Einstein A coefficient in s^{-1} and the radiative lifetimes τ for the $v' = 0$ and 1 vibrational levels of the $B^2\Sigma^+$ state to the vibrational levels of the $X^2\Pi$ state of the OH molecule.

		B–X transition			
$A_{v'v''}$		$v' = 0$	% Error	1	% Error
$v'' = 0$	a	3.199×10^{-1}		7.674×10^{-1}	
	b	2.400×10^{-1}	24.9	7.000×10^{-1}	8.8
	c	3.503×10^{-1}	8.7	8.385×10^{-1}	8.5
1	a	7.535×10^0		1.676×10^1	
	b	5.200×10^0	30.9	1.400×10^1	16.5
	c	8.367×10^0	9.9	1.858×10^1	9.8
2	a	8.093×10^1		1.659×10^2	
	b	5.600×10^1			
	c	9.077×10^1	30.8	1.400×10^2	15.6
3	a	5.523×10^2		1.032×10^3	
	b	3.900×10^2	29.4	0.850×10^3	17.7
	c	6.221×10^2	11.2	1.164×10^3	11.3
4	a	2.605×10^3		4.381×10^3	
	b	1.900×10^3	27.1	3.800×10^3	13.3
	c	2.920×10^3	10.8	4.929×10^3	11.1
5	a	8.983×10^3		1.332×10^4	
	b	7.000×10^3	22.1	1.200×10^4	9.9
	c	9.878×10^3	9.1	1.475×10^4	9.7
6	a	2.278×10^4		2.894×10^4	
	b	1.900×10^4	16.6	2.800×10^4	3.2
	c	2.413×10^4	5.6	3.096×10^4	6.5
7	a	4.181×10^4		4.351×10^4	
	b	3.700×10^4	11.5	4.500×10^4	3.3
	c	4.195×10^4	0.3	4.407×10^4	1.3
8	a	5.381×10^4		4.254×10^4	
	b	4.900×10^4	8.9	4.700×10^4	9.5
	c	5.074×10^4	5.7	4.027×10^4	5.3
9	a	4.491×10^4		2.321×10^4	
	b	4.300×10^4	4.2	2.700×10^4	14.0
	c	3.995×10^4	10.9	2.065×10^4	11.0
10	a	2.001×10^4		4.518×10^3	
	b	1.900×10^4	5.0	6.000×10^3	24.7
	c	1.666×10^4	16.7	3.873×10^3	14.3
11	a	2.373×10^3		2.396×10^{-1}	
	b	2.600×10^3	8.7	10.00×10^0	97.6
	c	1.440×10^3	39.3	3.404×10^{-1}	29.6
12	a	3.834×10^2		6.183×10^1	
	b	2.300×10^2	40.0	20.00×10^1	69.1
	c	7.438×10^2	48.5	3.984×10^1	35.6
13	a	1.152×10^3		1.025×10^3	
	b	1.000×10^3	13.2	0.590×10^3	42.4
	c	1.173×10^3	1.7	1.303×10^3	21.3
Sum (s^{-1}) = $A_{v'v''}$	a	1.994×10^5		1.627×10^5	
	b	1.800×10^5	9.7	1.706×10^5	4.6
	c	1.903×10^5	4.6	1.622×10^5	0.3
$\tau:(s) = 1/A_{v'v''}$ (ns)	a	5051.56		6815.48	
	d	5549.96	9.7	5861.50	4.6
	c	5254.24	4.6	6164.13	0.3

^aPresent work using this work's TDM with adding extra symmetries.^bLanghoff, *et al.* [1].^cUsing this work's PECs and Langhoff, *et al.*'s TDM (basis I).^dCalculated in this work using Langhoff, *et al.*'s [1] data.

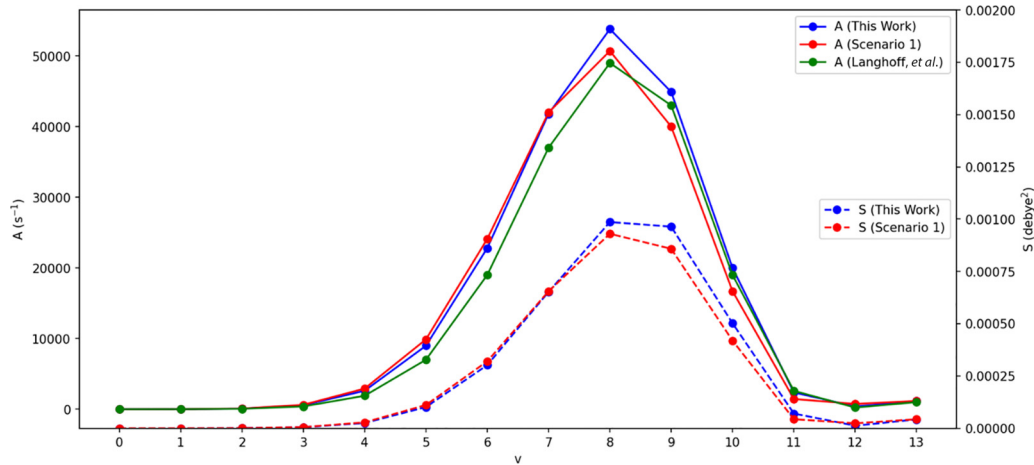


FIG. 4. The variation of Langhoff, *et al.*'s published and Scenario I results of Einstein A coefficients and line strength with those obtained in this work with respect to the vibration quantum number (v'').

The summed transition probability of the $B^2\Sigma^+$ into the discrete levels of the ground state $X^2\Pi$ is also calculated and presented in Table III, which shows percentage differences of 9.7% and 4.6%, respectively, as calculated with Langhoff, *et al.*'s published data.

It is worth noting that even though these results were obtained using a high level of *ab initio* calculations, the comparison of the spectroscopic constants of the $B^2\Sigma^+$ state did not show excellent agreement with the experimental values. Thus, the results of the $B^2\Sigma^+ - X^2\Pi$ transition could be improved by performing more accurate calculations, which would take into account considering the core-core and core-valence contributions in their electronic structure computations or by refining the *ab initio* PEC of the $B^2\Sigma^+$ state of OH by fitting it to experimental energies for achieving experimental accuracy.

There are no accurate values yet of the band Einstein A coefficients of the D-X transition of OH in the literature. Dishoeck, *et al.* [31] calculated the summed transition probabilities from $D^2\Sigma^-$ to the discrete levels of the ground state $X^2\Pi$ as $2.3 \times 10^8 \text{ s}^{-1}$ for $v' = 0$ and $2.4 \times 10^8 \text{ s}^{-1}$ for $v' = 1$ using basis set I PECs and basis set IA TDMF (defined in Sec. III B) and $1.5 \times 10^8 \text{ s}^{-1}$ for $v' = 0$ and $1.6 \times 10^8 \text{ s}^{-1}$ for $v' = 1$ using basis set II PEC and TDM (also defined in Sec. III B). In this work, we calculated the band Einstein A coefficient values for the $D^2\Sigma^- - X^2\Pi$ transition, as presented in Table IV.

To better compare our results with the literature, we calculated the band oscillator strengths (f_{value}) for the D-X (0-0) and (1-0) bands, using the formula

$$f_{\text{value}} = 1.499\,193\,68\,A_{v''v'}/v^2, \quad (4)$$

where $A_{v''v'}$ is the Einstein A coefficients (s^{-1}) and v is the wave number (in cm^{-1}).

The oscillator strengths are $f_{00} = 0.0125$ and $f_{10} = 0.0024$, for the 0-0 and 1-0 bands, respectively, showing good agreement with the theoretical values calculated by Heays, *et al.* [19] using Van der Loo, *et al.*'s [37] PECs and TDMCs, $f_{00} = 0.0127$ and $f_{10} = 0.0025$. Moreover, these values are in very good agreement with the values reported by Heays, *et al.*

[19] in their experiment, which cited $f_{00} = 0.0135 \pm 0.0010$ and $f_{10} = 0.0021 \pm 0.0003$. Additionally, the result of the 0-0 band is in good agreement with that calculated by Dishoeck, *et al.* [31] ($f_{00} = 0.012$) using basis set I (defined in Sec. III B) but is somewhat smaller than that of 1-0 band, in which they reported $f_{10} = 0.0044$.

The radiative lifetimes $\tau_{v'}$ for $B^2\Sigma^+ - X^2\Pi$ and $D^2\Sigma^- - X^2\Pi$ transitions were calculated using the following formula:

$$\tau_{v'} = \frac{1}{\sum_{v''} A_{v''v'}}. \quad (5)$$

The values of lifetimes are represented in Tables III and IV for $B^2\Sigma^+ - X^2\Pi$ and $D^2\Sigma^- - X^2\Pi$ transitions, respectively. In literature, all the computed lifetimes of $B^2\Sigma^+$ encompass the entire lifetime involving $B^2\Sigma^+ - X^2\Pi$, $B^2\Sigma^+ - A^2\Sigma^+$, and the continuum transition $B^2\Sigma^+ - 2^2\Pi$. No one seems to have solely calculated the specific lifetime of the transi-

TABLE IV. The Einstein A coefficient in s^{-1} and the radiative lifetimes τ for $v' = 0$ and 1 vibrational levels of the $D^2\Sigma^-$ state to the vibrational levels of the $X^2\Pi$ state of the OH molecule.

$A_{v''v'}$	$v' = 0$	1
$v'' = 0$	1.107×10^8	2.307×10^7
1	5.817×10^7	4.849×10^7
2	1.009×10^7	8.927×10^7
3	6.510×10^5	2.759×10^7
4	1.251×10^4	2.275×10^6
5	1.629×10^2	3.270×10^4
6	2.064×10^0	8.661×10^1
7	6.680×10^1	2.282×10^0
8	4.617×10^1	3.565×10^0
9	4.199×10^0	2.220×10^1
10	2.775×10^0	2.061×10^1
11	9.335×10^0	7.008×10^0
12	7.706×10^0	4.138×10^{-1}
13	3.421×10^0	4.941×10^{-1}
Sum (s^{-1}) = $A_{v''v'}$	1.796×10^8	1.907×10^8
τ (ns) = $1/A_{v''v'}$	5.568	5.243

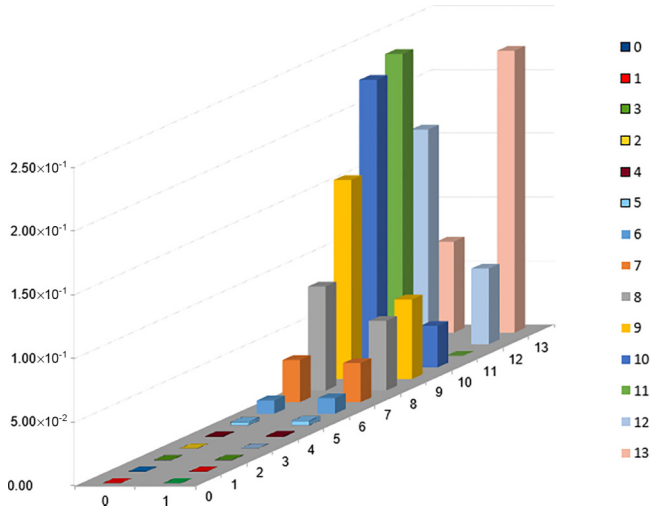


FIG. 5. Calculated FCFs of the $B^2\Sigma^+ - X^2\Pi$ transition of OH radical.

tion $B^2\Sigma^+ - X^2\Pi$. The radiative lifetimes of $B^2\Sigma^+ - X^2\Pi$ transition alone, based on Langhoff, *et al.*'s [1] Einstein A coefficients, using Eq. (2), are in agreement with those in this work and are displayed in Table III. The results obtained using Dishoeck, *et al.*'s [31] data are more or less in accordance with those obtained here, (4.35 ns for $v = 0$) and (4.17 ns for $v = 1$), probably due to the discrepancy in the TDM trends along the investigated internuclear range.

D. Franck-Condon factor

The Franck-Condon factors (FCFs) of $B^2\Sigma^+ - X^2\Pi$ and $D^2\Sigma^- - X^2\Pi$ transitions of OH radical between $0 \leq v' \leq 13$ and $0 \leq v'' \leq 1$ have been calculated considering only the vibrational levels using Le Roy's LEVEL program [56]. The data are reported in Tables TS1 and TS2, respectively, in the Supplemental Material [57]. To better understand their behavior, the FCF plotting is shown in Figs. 5 and 6, where

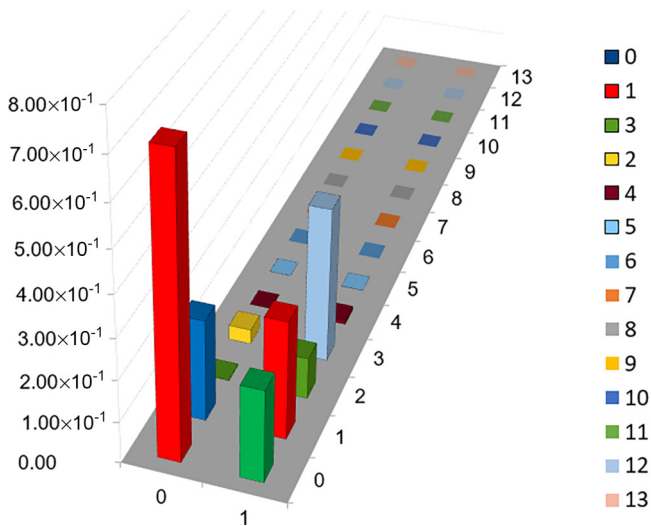


FIG. 6. Calculated FCFs of the $D^2\Sigma^- - X^2\Pi$ transition of OH radical.

both transitions are off diagonal. It is clear from Fig. 5 of $B^2\Sigma^+ - X^2\Pi$ transition that the FCFs start to show at $v'' = 6$ for the ground state. This is probably the reason why experimental spectra are available at this level and not at lower ones. Furthermore, these lower values of FCFs reveal the accuracy of the small Einstein A coefficient values obtained for these bands.

E. Spectra comparisons

1. OH $B^2\Sigma^+ \rightarrow X^2\Pi$

We show the intensities and positions of several lines for the (0–8) and (0–6) vibrational bands in the $B^2\Sigma^+ \rightarrow X^2\Pi$ emission spectra observed by Hwang, *et al.* [18] at a rotational temperature of 187 K in Figs. 7 and 8. We compare these spectra with the spectra calculated in this work using this work's PECs and TDM and using Langhoff, *et al.*'s [1] PECs and TDM to compute the TDMMEs, along with Bernath's [24] molecular constants to account for the wave number. The results show an excellent agreement in the line position; however, some peaks differ in intensity. Many effects might contribute to the differences in peak intensities between our spectral data, the spectra calculated using Langhoff, *et al.*'s [1] PECs and TDM, and the observed one by Hwang, *et al.* [18]. First, the reason behind the difference between our spectra and those obtained using Langhoff, *et al.*'s data is that the intensities depend on the values of the Einstein A coefficient, for which differences were justified in Sec. II C. As an illustration, our spectra of the B–X (0–8) vibrational band give good correspondence with Langhoff, *et al.*'s intensities, as shown in Fig. 7. This is due to the agreement in the values of the Einstein A coefficient at this band. For the B–X (0–6) band, the value of the Einstein A coefficient in our work for this transition differs from the calculated value by Langhoff, *et al.* [1], with a percentage difference of 16.6%. This discrepancy is the main reason for the difference in the intensities of many of the peaks in that vibrational band. At the same time, our spectra show better agreement with Hwang than those using Langhoff, *et al.*'s data for a majority of the peaks, such as $Q_{11\text{ef}}$ ($J'' = 7/2, 3/2$), $Q_{21\text{ff}}$ ($J'' = 7/2, 5/2, 3/2$), and $P_{11\text{ee}}$ ($J'' = 5/2, 3/2$).

Furthermore, Sappey, *et al.* [20] measured the ratio of the two observed bands of the B–X system, where the experimental result is $I(0, 9)/I(0, 10) = 2.0 \pm 1.0$, which is in good agreement with our calculated value (of 2.1) and Langhoff, *et al.*'s theoretical value (of 2.3). The same authors mentioned the difficulty in calculating the weak transitions of the higher vibrational levels ($v \geq 10$) of the $X^2\Pi$ state because it requires determining the relative magnitude of two different electronic transition moments.

The discrepancy between our calculated spectra and the experimental spectra obtained by Hwang, *et al.* [18] could be due to experimental conditions, such as calibration issues or perturbations of the $B^2\Sigma^+$ state. In fact, Hwang, *et al.* [18] mentioned that the experiment was initially designed to avoid collisional relaxation of the nascent OH, but the spectral analysis revealed that collisions did occur, causing partial relaxation of vibrational populations. This relaxation could result in the energy levels of the OH being partially redistributed to other vibrational states during the

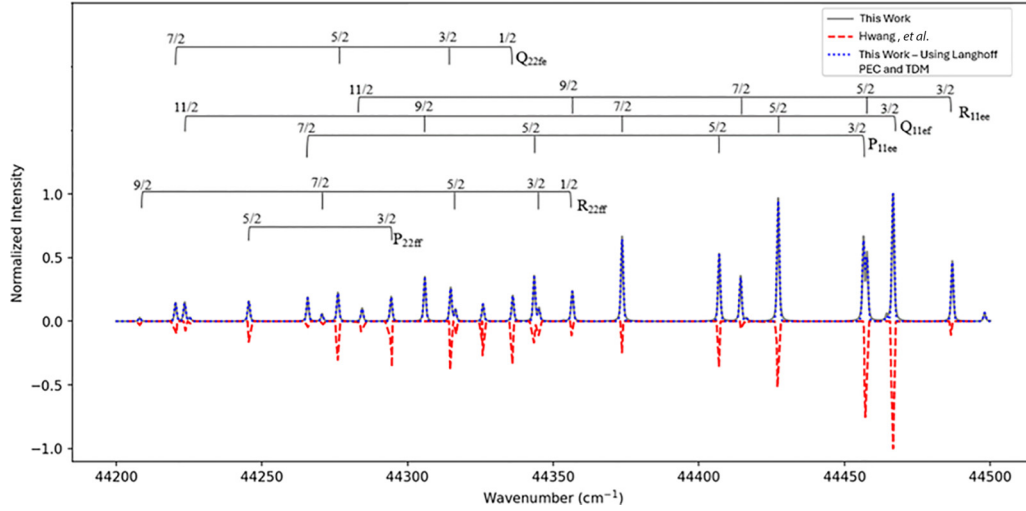


FIG. 7. Comparison between the spectra calculated in this work using our investigated PECs and TDMFs, the observed B–X (0–8) spectra of OH by Hwang, *et al.* [18], and the spectra calculated using the PECs of Langhoff, *et al.* [1] in this study.

collisional relaxation process and rotational populations being equilibrated to approximately room temperature. The collisional relaxation could affect the intensity of spectral lines by causing line broadening, altering line shapes, redistributing intensity among transitions, and overall modifying the spectral profile [71]. Thus, the above mentioned effects can explain the discrepancy in the intensities for some of the detected 0–6 and 0–8 transitions.

2. $OH D^2\Sigma^- \leftarrow X^2\Pi$

Similarly, we compare the peak intensity and line positions of several lines of the simulated absorption $D^2\Sigma^- \leftarrow X^2\Pi$ spectra with the observed one by Heays, *et al.* [19] at a rotational temperature of (395 ± 7) K. The comparisons of the (0–0) and (1–0) vibrational bands spectra, presented in

Figs. 9 and 10, respectively, show excellent agreement in terms of wave number; this suggests that the theoretical model successfully captures the fundamental characteristics of the observed spectra. Additionally, the comparison of the line intensity of 0–0 bands presented in Fig. 9 shows good agreement. To enhance the clarity of the comparison, we subtracted the background from the initial published figure of Heays, *et al.* [19] by selecting background regions of the spectrum and then subtracting them from the entire spectrum. This process allowed us to isolate the absorption features more effectively, ensuring a more accurate comparison between the spectra. Furthermore, the comparison of the line intensities of the 1–0 bands shown in Fig. 10 reveals good agreement. However, we noticed that certain peaks of the 1–0 bands at higher rotational levels, which are present in the spectra of Heays, *et al.* [19], were not identified by them, likely because they did not calculate these higher rotational levels. We have

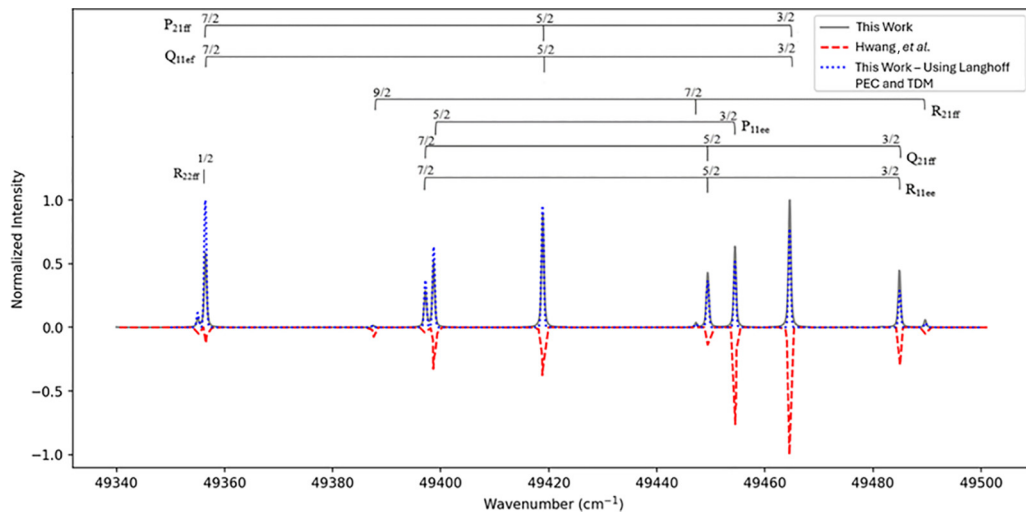


FIG. 8. Comparison between the spectra calculated in this work using our investigated PECs and TDMFs, the observed B–X (0–6) spectra of OH by Hwang, *et al.* [18], and the spectra calculated using the PECs of Langhoff, *et al.* [1] in this study.

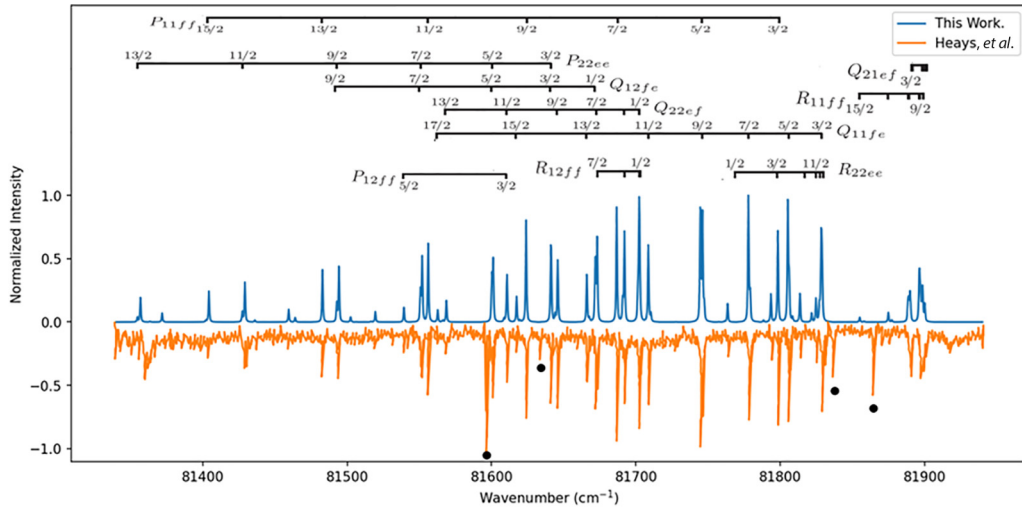


FIG. 9. Comparison between the D-X (0-0) spectra calculated in this work and that by Heays, *et al.* [19]. Noting that the spectrum of Heays, *et al.* was shifted and normalized for the sake of visualization. The black circle denotes the H₂ absorption lines observed in Heays' spectrum.

attempted to assign these peaks to our spectra, as shown in red.

F. MARVEL analysis data comparison

In general, the assessment of the accuracy of a molecule's rovibrational energy levels obtained through our line lists calculation is a rather complicated task, given the multitude of available experimental data with which to compare. In this case, a possible solution is to compare the energy levels obtained with the MARVEL method. The MARVEL approach [72–74] is a technique used to convert a given set of experimental transition frequencies into empirical energy levels. During this conversion, the uncertainties linked to the input transition data are considered and carried forward to the resulting energy levels. This process relies on the creation of

experimental SNs [71,75–77] that contain all interconnected transitions. Specific descriptors are employed to differentiate the rovibronic states of OH through this approach. These descriptors consist of the electronic state, the vibrational quantum number level (v), the total angular momentum quantum number without nuclear spin (J), the rotationless parity (e/f), and the spin components (F_1 and F_2).

Furtenbacher, *et al.* have published an extensive MARVEL analysis of the OH molecule [3] that contains 15 938 measured transitions of the $X^2\Pi - X^2\Pi$, $A^2\Sigma^+ - X^2\Pi$, $B^2\Sigma^+ - X^2\Pi$, $B^2\Sigma^+ - A^2\Sigma^+$, and $C^2\Sigma^+ - A^2\Sigma^+$ of ¹⁶OH. This analysis resulted in a total of 1624 empirical rovibronic energy levels to the $X^2\Pi$, $A^2\Sigma^+$, $B^2\Sigma^+$, and $C^2\Sigma^+$ states. In the current work, modifications have been done for the entries of $B^2\Sigma^+ - X^2\Pi$ and $B^2\Sigma^+ - A^2\Sigma^+$ transitions sourcing from Copeland, *et al.* [23] and Sappey, *et al.* [36], to account for calculated term

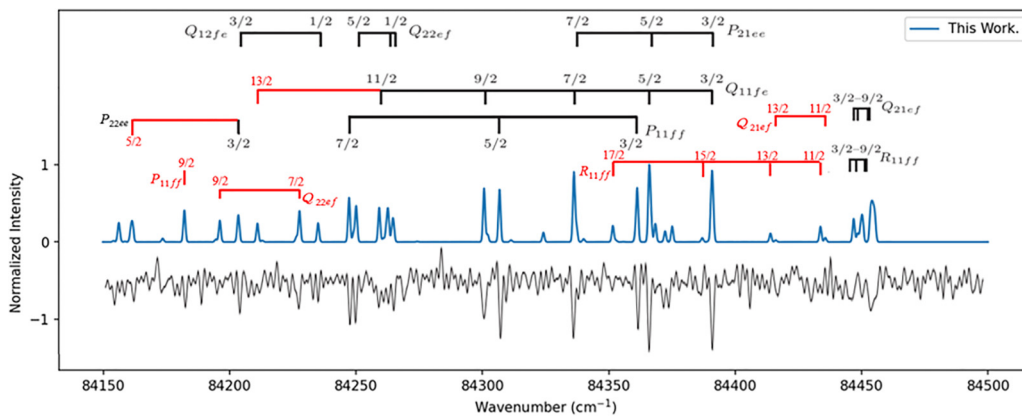


FIG. 10. Comparison between the D-X (1-0) spectra calculated in this work and that by Heays, *et al.* [19]. The black assignments originate from Heays *et al.*, while the red ones are deduced from this work.

TABLE V. MARVEL and calculated term values (cm^{-1}) of $\text{B}^2\Sigma^+$ ($v = 0, 1$) state of OH radical with respect to the $\text{X}^2\Pi$ ($v = 0$) F_{1e} ($J = 1.5$) level.

Type	$v = 0$				$v = 1$			
	MARVEL		Calculated		MARVEL		Calculated	
	J	F_{1e}	F_{2f}	F_{1e}	F_{2f}	F_{1e}	F_{2f}	F_{1e}
0.5	68 406.299 29	68 416.460 94	68 406.302 03	68 416.447 54	69 066.1188	69 074.138 44	69 066.133 33	69 074.339 44
1.5	68 416.4902	68 436.766 59	68 416.486 98	68 436.755 86	69 074.336 63	69 090.656 16	69 074.339 44	69 090.636 36
2.5	68 436.821 05	68 467.163 52	68 436.821 2	68 467.168 92	69 090.697 63	69 115.022 55	69 090.688 54	69 114.999 32
3.5	68 467.2615	68 507.6199	68 467.259 56	68 507.618 63	69 115.103 33	69 147.202 94	69 115.069 47	69 147.212 86
4.5	68 507.740 93	68 618.239 09	68 507.733 76	68 618.234 52	69 147.296 25	69 186.993 62	69 147.298 09	69 186.999 52
5.5	68 558.154 82	68 767.560 58	68 558.151 45	68 767.557 05	69 187.091 12	69 233.950 91	69 187.0961	69 233.9595
6.5	68 618.391 65	68 558.008 39	68 618.3952	68 558.0129	69 234.057 84	69 287.545 94	69 234.062 87	69 287.535 41
7.5	68 767.764 27	68 688.134 68	68 767.757 14	68 688.139 84	69 287.645 76	69 346.956 94		
8.5	68 688.32084	68 856.283 24	68 688.3211	68 856.284 35	69 347.056 93	69 409.110 21		
9.5	68 856.503 14	68 954.089 98	68 856.501 26	68 954.087 69	69 409.092 54	–		
10.5	68 954.338 77	–	68 954.319 19	–	–	–		

values initially presented by Bernath, *et al.* [24]. In total, 171 lines were updated from the first source and 8 from the second.

At the same time, a preliminary investigation of the MARVEL transitions involving the $\text{D}^2\Sigma^-$ state is presented in this work. Table TS3 of the Supplemental Material [57] lists the available work in the literature that has not been considered by Furtenbacher, *et al.* [3] on OH molecule emission properties. From the list, and up to our knowledge, only two sources contain experimental data on transitions involving the $\text{D}^2\Sigma^-$ states: Douglas [29] and Heays, *et al.* [19]. The last provided term values for $v = 0$ and $v = 1$ of $\text{D}^2\Sigma^-$, but only for the rotational levels $J = 0.5$ to $J = 5.5$. Douglas [29] did provide energy levels up to $J' = 17.5$, but for $v = 0$ only. Additionally, the first reported an uncertainty of 0.01 cm^{-1} , while the second indicated that the relative error for the highly accurate lines exceeds 0.05 cm^{-1} , but with more significant errors observed for overlapping lines. To avoid any risks, we assumed Douglas' uncertainty to be 0.5 cm^{-1} in our MARVEL analysis. One has to note that practically, two sources are usually insufficient to create an accurate MARVEL dataset, especially when there is scarce overlap between them; however, we are using this method here as a means to crudely assess the precision of the energy levels obtained in this work. A much deeper investigation is planned in the future as more experimental transitions involving this state are made available. Still, a comparison between this work's MARVEL $\text{D}^2\Sigma^-$ state energy levels, and those reported by Heays, *et al.* [19], as calculated using effective Hamiltonians to fit the observed transitions, shows deviations that are less than 0.0035 cm^{-1} for all of the energy values, whether one considers Heays' transitions only or those of Heays' and Douglas' combined, in the MARVEL process. This is a possible indicator for a homogeneity in both Heays and Douglas' transitions.

Overall, with this method, a total of 46 approximate empirical energy levels of the $\text{D}^2\Sigma^-$ state are determined in the SN, derived from 212 measured $\text{D}^2\Sigma^- - \text{X}^2\Pi$ transitions. The obtained empirical energy levels of the $\text{X}^2\Pi$ and $\text{A}^2\Sigma^+$ states are in accordance with the previously published work

of Furtenbacher, *et al.*, as very similar results are obtained through comparisons with *MoLLIST* [78]. The updated term values of the $\text{B}^2\Sigma^+$ and $\text{D}^2\Sigma^+$ electronic states of OH resulting from the analysis are displayed in Tables V and VI, respectively. The transitions file and the energy levels of this study are available in the Supplemental Material [57].

G. Comparison of our line list results and our MARVEL analysis for B–X and D–X transitions

The comparison of the theoretical energy levels of $\text{B}^2\Sigma^+$ state of OH, obtained in this study from the calculation of line lists, with the empirical (MARVEL) rovibronic energy shows an excellent agreement with a deviation of less than 0.035 cm^{-1} , as shown in Fig. 11. This supports that the molecular constants obtained by Bernath, *et al.* [24] are very accurate and align well with the line positions of $\text{B}^2\Sigma^+ - \text{X}^2\Pi$ transition.

For the $\text{D}^2\Sigma^-$ state of OH, when comparing our theoretical energy levels obtained using line lists with the empirical

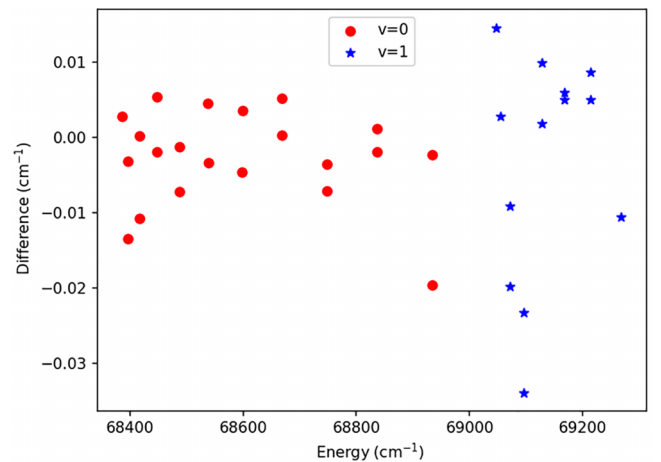


FIG. 11. Differences between the updated MARVEL energy levels of the $\text{B}^2\Sigma^+$ state and the energy levels obtained in this study.

TABLE VI. MARVEL and calculated term values (cm^{-1}) of $D^2\Sigma^-$ ($v = 0, 1$) state of OH radical with respect to the $X^2\Pi$ ($v = 0$) F_{1e} ($J = 1.5$) level.

Type	$v = 0$				$v = 1$			
	MARVEL		Calculated		MARVEL		Calculated	
J	F_{1f}	F_{2e}	F_{1f}	F_{2e}	F_{1f}	F_{2e}	F_{1f}	F_{2e}
0.5	81 798.216 27	81 828.987 18	81 798.241 51	81 828.986 83	84 361.405 31	84 391.278 11	84 361.404 38	84 391.277 5
1.5	81 828.461 55	81 889.954 47	81 828.463 54	81 889.907 43	84 390.828 65	84 450.533 27	84 390.827 5	84 450.532 46
2.5	81 889.092 06	81 981.228 16	81 889.057 85	81 981.110 97	84 449.784 03	84 539.237 85	84 449.782 46	84 539.236 7
3.5	81 980.015 43	82 102.395 02	81 979.961 56	82 102.500 49	84 538.189	84 657.267 61	84 538.186 7	84 657.266 38
4.5	82 101.030 45	82 253.964 22	82 101.073 45	82 253.953 26	84 655.918 97	84 804.458 18	84 655.916 38	84 804.456 38
5.5	82 252.273 79	82 435.412 47	82 252.251 73	82 435.322 92	84 802.809 04	84 980.601 36	84 802.806 38	84 980.600 3
6.5	82 433.372 7	82 646.373 11	82 433.311 89	82 646.441 41	—	—	—	—
7.5	82 643.880 11	82 886.745 58	82 644.024 46	82 887.121 02	—	—	—	—
8.5	82 884.057 28	83 157.088 64	82 884.112 74	83 157.156 35	—	—	—	—
9.5	83 153.240 31	83 453.992 05	83 153.250 61	83 456.326 26	—	—	—	—
10.5	83 451.075 63	83 780.279 57	83 451.060 19	83 784.395 82	—	—	—	—
11.5	83 776.896 74	84 134.446 29	83 777.109 57	84 141.118 22	—	—	—	—
12.5	84 130.936 56	84 516.578 57	84 130.910 46	84 526.236 67	—	—	—	—
13.5	84 512.174 62	84 924.878 06	84 511.915 91	84 939.486 28	—	—	—	—
14.5	84 920.450 07	85 359.603 69	84 919.517 89	85 380.595 88	—	—	—	—
15.5	85 355.228 42	87 305.750 5	85 353.044 94	81 828.986 83	—	—	—	—
16.5	85 815.493 09	81 828.987 18	81 798.241 51	81 889.907 43	—	—	—	—

rovibronic energy levels of MARVEL, an excellent agreement is observed for $v = 1$ ($J \leq 5.5$) with energy difference less than 0.002 cm^{-1} . Similarly for $v = 0$ at lower rovibrational levels ($J \leq 10.5$), a good agreement is observed with a deviation of less than 0.5 cm^{-1} . However, as we explore higher rovibrational levels (up to $J = 14.5$), the deviation gradually becomes more pronounced, especially for energy values with F_{2e} , however, less deviation is obtained with the analogous energy levels with F_{1f} , as illustrated in Fig. 12. This difference probably arises from the molecular constants taken from Heays, *et al.* [19] for the D ($v = 0$) level, where he mentioned that these constants do not accurately reproduce the perturbed spectrum within experimental accuracy as a result of the local perturbation mentioned in Sec. III A. We believe that at higher rovibrational levels, the energy levels obtained through

MARVEL are more reliable than the ones calculated in our line lists using Heays' molecular constants. To address this, we exclude the high rovibrational levels from our calculations and limit our analysis to $J \leq 10.5$.

IV. CONCLUSION

Extensive line lists for the $B^2\Sigma^+ - X^2\Pi$ and $D^2\Sigma^- - X^2\Pi$ transitions of the OH radical have been computed, starting from the calculation of potential energy curves and transition dipole moment functions obtained from high-level *ab initio* study of the electronic structure of OH using CASSCF/MRCI + Q methods with a large basis set and extensive electron correlation. These line lists are obtained by combining theoretical line intensities calculated in this work with observed line positions reported in the literature. Furthermore, an updated MARVEL analysis for OH has been conducted, resulting in updating the empirical rovibronic energy levels for the $B^2\Sigma^+$ state and the determination of empirical rovibronic energy levels for the $D^2\Sigma^-$ state. These energy levels demonstrate a high level of agreement when compared to our calculated energy levels from the line lists, as well as values reported in the literature. The present calculated data of line lists for OH can be highly valuable in identifying molecular structure, measuring molecular abundances, and probing its chemical bond nature.

ACKNOWLEDGMENTS

This work was financially supported by the ASPIRE Award for Research Excellence (AARE20-00031) and the Khalifa University internal research grant RIG-2024-053. Almesbar high performance computer was used to complete this re-

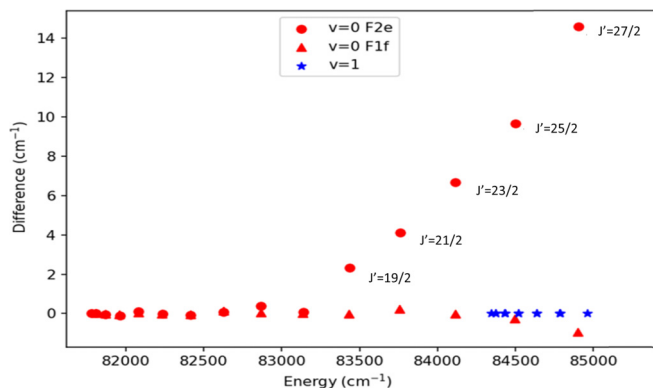


FIG. 12. Differences between the MARVEL energy levels of the $D^2\Sigma^-$ state and the energy levels obtained in this study.

search. This work was done using a Python script program for Hund's b to Hund's a transformation developed by James H. and with support provided through private communication with Professor Peter F. Bernath and Dr. Mahdi Yousefi.

DATA AVAILABILITY

The data supporting this study's findings are available within the article.

- [1] S. R. Langhoff, E. F. van Dishoeck, R. Wetmore, and A. Dalgarno, Radiative lifetimes and dipole moments of the $A^2\Sigma^+$, $B^2\Sigma^+$, and $C^2\Sigma^+$ states of OH, *J. Chem. Phys.* **77**, 1379 (1982).
- [2] M. Yousefi, P. F. Bernath, J. Hodges, and T. Masseron, A new line list for the $A^2\Sigma^+ - X^2\Pi$ electronic transition of OH, *J. Quant. Spectrosc. Radiat. Transf.* **217**, 416 (2018).
- [3] T. Furtenbacher, S. T. Hegedus, J. Tennyson, and A. G. Császár, Analysis of measured high-resolution doublet rovibronic spectra and related line lists of ^{12}CH and ^{16}OH , *Phys. Chem. Chem. Phys.* **24**, 19287 (2022).
- [4] J. Lelieveld, F. J. Dentener, W. Peters, and M. C. Krol, On the role of hydroxyl radicals in the self-cleansing capacity of the troposphere, *Atmos. Chem. Phys.* **4**, 2337 (2004).
- [5] M. Gacesa and V. Kharchenko, Quantum reactive scattering of $\text{O}(^3\text{P}) + \text{H}_2$ at collision energies up to 4.4 eV, *J. Chem. Phys.* **141**, 164324 (2014).
- [6] M. Gacesa, N. Lewkow, and V. Kharchenko, Non-thermal production and escape of OH from the upper atmosphere of Mars, *Icarus* **284**, 90 (2017).
- [7] I. A. B. Meinel, OH emission bands in the spectrum of the night sky, *Astrophys. J.* **111**, 555 (1950).
- [8] M. C. Abrams, S. P. Davis, M. L. P. Rao, R. Engleman, Jr., and J. W. Brault, High-resolution Fourier transform spectroscopy of the Meinel system of OH, *Astrophys. J. Suppl. Ser.* **93**, 351 (1994).
- [9] A. Goldman, W. G. Schoenfeld, D. Goorvitch, C. Chackerian, Jr., H. Dothe, F. Mélen, M. C. Abrams, and J. E. A. Selby, Updated line parameters for OH $X^2\Pi - X^2\Pi$ ($v'' v'$) transitions, *J. Quant. Spectrosc. Radiat. Transf.* **59**, 453 (1998).
- [10] J. S. A. Brooke, P. F. Bernath, C. M. Western, C. Sneden, M. Afşar, G. Li, and I. E. Gordon, Line strengths of rovibrational and rotational transitions in the $X^2\Pi$ ground state of OH, *J. Quant. Spectrosc. Radiat. Transf.* **168**, 142 (2016).
- [11] D. R. Crosley and R. K. Lengel, Relative transition probabilities and the electronic transition moment in the A-X system of OH, *J. Quant. Spectrosc. Radiat. Transf.* **15**, 579 (1975).
- [12] C. C. Wang and D. K. Killinger, Effect of rotational excitation on the band oscillator strength of OH, *Phys. Rev. A* **20**, 1495 (1979).
- [13] J. A. Coxon, Optimum molecular constants and term values for the $X^2\Pi$ ($v \leq 5$) and $A^2\Sigma^+$ ($v \leq 3$) states of OH, *Can. J. Phys.* **58**, 933 (1980).
- [14] R. Engleman, Accurate wavenumbers of the $A^2\Sigma \rightarrow X^2\Pi$ (0, 0) and (1, 0) bands of OH and OD, *J. Quant. Spectrosc. Radiat. Transf.* **12**, 1347 (1972).
- [15] G. H. Dieke and H. M. Crosswhite, The ultraviolet bands of OH fundamental data, *J. Quant. Spectrosc. Radiat. Transf.* **2**, 97 (1962).
- [16] C. W. Bauschlicher and S. R. Langhoff, Theoretical determination of the radiative lifetime of the $A^2\Sigma^+$ state of OH, *J. Chem. Phys.* **87**, 4665 (1987).
- [17] A. C. P. Bittencourt, F. V. Prudente, and J. D. M. Vianna, The fitting of potential energy and transition moment functions using neural networks: Transition probabilities in OH ($A^2\Sigma^+ \rightarrow X^2\Pi$), *Chem. Phys.* **297**, 153 (2004).
- [18] E. S. Hwang, J. B. Lipson, R. W. Field, and J. A. Dodd, Detection of OH (X, v'', J'') via the $B^2\Sigma^+ - X^2\Pi$ transition and properties of the $B^2\Sigma^+$ State, *J. Phys. Chem. A* **105**, 6030 (2001).
- [19] A. N. Heays, N. de Oliveira, B. Gans, K. Ito, S. Boyé-Péronne, S. Douin, K. M. Hickson, L. Nahon, and J. C. Loison, High-resolution one-photon absorption spectroscopy of the $D^2\Sigma^- \leftarrow X^2\Pi$ system of radical OH and OD, *J. Quant. Spectrosc. Radiat. Transf.* **204**, 12 (2018).
- [20] A. D. Sappey and R. A. Copeland, Laser double-resonance study of OH ($X^2\Pi_i, v = 12$), *J. Mol. Spectrosc.* **143**, 160 (1990).
- [21] J. A. Coxon, A. D. Sappey, and R. A. Copeland, Molecular constants and term values for the hydroxyl radical, OH: The $X^2\Pi$ ($v = 8, 12$), $A^2\Sigma^+$ ($v = 4-9$), $B^2\Sigma^+$ ($v = 0, 1$), and $C^2\Sigma^+$ ($v = 0, 1$) states, *J. Mol. Spectrosc.* **145**, 41 (1991).
- [22] R. A. Copeland, J. B. Jeffries, and D. R. Crosley, The OH $A^2\Sigma^+ - X^2\Pi_i$ (4, 2) band: Line positions and linewidths, *J. Mol. Spectrosc.* **143**, 183 (1990).
- [23] R. A. Copeland, B. R. Chalamala, and J. A. Coxon, Laser-induced fluorescence of the $B^2\Sigma^+ - X^2\Pi$ system of oh: Molecular constants for $B^2\Sigma^+$ ($v = 0, 1$) and $X^2\Pi$ ($v = 7-9, 11-13$), *J. Mol. Spectrosc.* **161**, 243 (1993).
- [24] P. F. Bernath and R. Colin, Revised molecular constants and term values for the $X^2\Pi$ and $B^2\Sigma^+$ states of OH, *J. Mol. Spectrosc.* **257**, 20 (2009).
- [25] P. F. Bernath, The atmospheric chemistry experiment (ACE), *J. Quant. Spectrosc. Radiat. Transf.* **186**, 3 (2017).
- [26] P. F. Bernath, *et al.*, Atmospheric chemistry experiment (ACE): Mission overview, *Geophys. Res. Lett.* **32**, L15S01 (2005).
- [27] X. Qin and S. D. Zhang, Low-lying electronic states of the OH radical: Potential energy curves, dipole moment functions, and transition probabilities, *J. Korean Phys. Soc.* **65**, 2017 (2014).
- [28] B. S. D. R. Vamhindi and M. Nsangou, Accurate *ab initio* potential energy curves and spectroscopic properties of the low-lying electronic states of OH^- and SH^- molecular anions, *Mol. Phys.* **114**, 2204 (2016).
- [29] A. E. Douglas, Absorption of OH in the 1200 Å region, *Can. J. Phys.* **52**, 318 (1974).
- [30] E. F. van Dishoeck and A. Dalgarno, Photodissociation processes in the OH molecule, *J. Chem. Phys.* **79**, 873 (1983).
- [31] E. F. van Dishoeck, S. R. Langhoff, and A. Dalgarno, The low-lying $^2\Sigma^-$ states of OH, *J. Chem. Phys.* **78**, 4552 (1983).
- [32] M. Collard, P. Kerwin, and A. Hodgson, Two-photon resonance ionisation spectroscopy of OH/OD $D^2\Sigma^-$, *Chem. Phys. Lett.* **179**, 422 (1991).
- [33] E. de Beer, M. P. Koopmans, C. A. de Lange, Y. Wang, and W. A. Chupka, (2+1) Resonance-enhanced multipho-

- ton ionization–photoelectron spectroscopy of the OH radical, *J. Chem. Phys.* **94**, 7634 (1991).
- [34] C. McRaven, J. Alnis, B. Furneaux, and N. Shafer-Ray, A 1+1 ionization scheme for sensitive detection of the OH radical, *J. Phys. Chem. A* **107**, 7138 (2003).
- [35] M. E. Greenslade, M. I. Lester, D. Č. Radenović, A. J. A. van Roij, and D. H. Parker, (2+1) Resonance-enhanced ionization spectroscopy of a state-selected beam of OH radicals, *J. Chem. Phys.* **123**, 074309 (2005).
- [36] A. D. Sappey, D. R. Crosley, and R. A. Copeland, Laser-induced fluorescence in the $B^2\Sigma^+ - X^2\Pi_i$ system of OH, *AIP Conf. Proc.* **191**, 645 (1989).
- [37] M. P. J. van der Loo and G. C. Groenenboom, *Ab initio* calculation of (2+1) resonance enhanced multiphoton ionization spectra and lifetimes of the (D, 3) $^2\Sigma^-$ states of OH and OD, *J. Chem. Phys.* **123**, 074310 (2005).
- [38] A. Tappe, C. J. Lada, J. H. Black, and A. A. Muench, Discovery of superthermal hydroxyl (OH) in the HH 211 outflow, *Astrophys. J.* **680**, L117 (2008).
- [39] S. Noll, W. Kausch, S. Kimeswenger, S. Unterguggenberger, and A. M. Jones, OH populations and temperatures from simultaneous spectroscopic observations of 25 bands, *Atmos. Chem. Phys.* **15**, 3647 (2015).
- [40] M. Asplund and A. E. G. Pérez, On OH line formation and oxygen abundances in metal-poor stars, *Astron. Astrophys.* **372**, 2 (2001).
- [41] A. A. Neuber, J. Janicka, and E. P. Hassel, Thermally assisted fluorescence of laser-excited OH $A^2\Sigma^+$ as a flame diagnostic tool, *Appl. Opt.* **35**, 4033 (1996).
- [42] R. Schiessl, U. Maas, A. Hoffmann, J. Wolfrum, and C. Schulz, Method for absolute OH-concentration measurements in premixed flames by LIF and numerical simulations, *Appl. Phys. B* **79**, 759 (2004).
- [43] C. Copeland, J. Friedman, and M. Renksizbulut, Planar temperature imaging using thermally assisted laser induced fluorescence of OH in a methane–air flame, *Exp. Therm. Fluid Sci.* **31**, 221 (2007).
- [44] W. H. Smith and T. P. Snow, Jr., Copernicus observational searches for OH and H₂O in diffuse clouds, *Astrophys. J.* **228**, 435 (1979).
- [45] M. Asplund, N. Grevesse, A. J. Sauval, C. A. Prieto, and D. Kiselman, Line formation in solar granulation – IV. [O I], O I and OH lines and the photospheric O abundance, *Astron. Astrophys.* **417**, 751 (2004).
- [46] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, Molpro: A general-purpose quantum chemistry program package, *WIREs Comput. Mol. Sci.* **2**, 242 (2012).
- [47] H.-J. Werner and P. J. Knowles, An efficient internally contracted multiconfiguration–reference configuration interaction method, *J. Chem. Phys.* **89**, 5803 (1988).
- [48] D. Feller, Application of a convergent, composite coupled cluster approach to bound state, adiabatic electron affinities in atoms and small molecules, *J. Chem. Phys.* **144**, 014105 (2016).
- [49] M. Semenov, N. El-Kork, S. N. Yurchenko, and J. Tennyson, Rovibronic spectroscopy of PN from first principles, *Phys. Chem. Chem. Phys.* **23**, 22057 (2021).
- [50] M. Korek, S. Bleik, and A. R. Allouche, Theoretical calculation of the low lying electronic states of the molecule NaCs with spin-orbit effect, *J. Chem. Phys.* **126**, 124313 (2007).
- [51] N. El-Kork, A. AlMasri Alwan, N. Abu El Kher, J. Assaf, T. Ayari, E. Alhseinat, and M. Korek, Laser cooling with intermediate state of spin–orbit coupling of LuF molecule, *Sci. Rep.* **13**, 7087 (2023).
- [52] I. Zeid, R. Al Abdallah, N. El-Kork, and M. Korek, *Ab initio* calculations of the electronic structure of the alkaline earth hydride anions XH^- ($X = \text{Mg, Ca, Sr and Ba}$) toward laser cooling experiment, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **224**, 117461 (2020).
- [53] F. Mélen, A. J. Sauval, N. Grevesse, C. B. Farmer, Ch. Servais, L. Delbouille, and G. Roland, A new analysis of the OH radical spectrum from solar infrared observations, *J. Mol. Spectrosc.* **174**, 490 (1995).
- [54] M. C. Abrams, A. Goldman, M. R. Gunson, C. P. Rinsland, and R. Zander, Observations of the infrared solar spectrum from space by the ATMOS experiment, *Appl. Opt.* **35**, 2747 (1996).
- [55] C. M. Western, PGOPHER: A program for simulating rotational, vibrational and electronic spectra, *J. Quant. Spectrosc. Radiat. Transf.* **186**, 221 (2017).
- [56] R. J. Le Roy, LEVEL: A computer program for solving the radial Schrödinger equation for bound and quasibound levels, *J. Quant. Spectrosc. Radiat. Transf.* **186**, 167 (2017).
- [57] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/h853-qnjt> for datasets accompanying this work: transitions, energy levels, FCFs, and comprehensive OH line lists.
- [58] A. Kramida, Yu. Ralchenko, J. Reader, and NIST ASD Team, NIST Atomic Spectra Database (version 5.12), NIST Standard Reference Database 78 (National Institute of Standards and Technology, Gaithersburg, MD, 2024), <https://physics.nist.gov/asd>.
- [59] F. Jensen, *Introduction to Computational Chemistry* (John Wiley & Sons, 2017).
- [60] D. Robinson, Splitting multiple bonds: A comparison of methodologies on the accuracy of bond dissociation energies, *J. Comput. Chem.* **34**, 2625 (2013).
- [61] J. M. L. Martin, J. P. François, and R. Gijbels, On size-consistency corrections for limited configuration-interaction calculations, *Chem. Phys. Lett.* **172**, 346 (1990).
- [62] G. B. Mitev, J. Tennyson, and S. N. Yurchenko, Predissociation dynamics of the hydroxyl radical (OH) based on a five-state spectroscopic model, *J. Chem. Phys.* **160**, 144110 (2024).
- [63] R. F. Barrow, The $B^2\Sigma^+ - A^2\Sigma^+$ Band-Systems of OH and OD, *Ark. Fys.* **11**, 281 (1956).
- [64] K. P. Huber and G. Herzberg, Constants of diatomic molecules, in *Molecular Spectra and Molecular Structure: IV. Constants of Diatomic Molecules*, edited by K. P. Huber and G. Herzberg (Springer, US, Boston, MA, 1979), pp. 8–689.
- [65] C. Carlone and F. W. Dalby, Spectrum of the hydroxyl radical, *Can. J. Phys.* **47**, 18 (1969).
- [66] G. B. Mitev, C. A. Bowesman, J. Zhang, S. N. Yurchenko, and J. Tennyson, ExoMol line lists–LXI. A trihybrid line list for Rovibronic transitions of the hydroxyl radical (OH), *Mon. Not. R. Astron. Soc.* **536**, 3401 (2025).
- [67] S. Srivastava and N. Sathyamurthy, *Ab initio* potential energy curves for the ground and low-lying excited states of OH and OH[−] and a study of rotational fine structure in photodetachment, *J. Phys. Chem. A* **118**, 6343 (2014).

- [68] J. Tellinghuisen and C. S. Ewig, *Ab initio* studies of molecular anions stabilized in point-charge lattices: Excited electronic states of OH^- , *Chem. Phys. Lett.* **165**, 355 (1990).
- [69] J. M. L. Martin, Spectroscopic quality *ab initio* potential curves for CH, NH, OH and HF. A convergence study, *Chem. Phys. Lett.* **292**, 411 (1998).
- [70] J. P. Maillard, J. Chauville, and A. W. Mantz, High-resolution emission spectrum of OH in an oxyacetylene flame from 3.7 to $0.9\ \mu\text{m}$, *J. Mol. Spectrosc.* **63**, 120 (1976).
- [71] T. Furtenbacher, P. Árendás, G. Mellau, and A. G. Császár, Simple molecules as complex systems, *Sci. Rep.* **4**, 4654 (2014).
- [72] A. G. Császár, G. Czakó, T. Furtenbacher, and E. Mátyus, An active database approach to complete rotational–vibrational spectra of small molecules, in *Annual Reports in Computational Chemistry*, edited by D. C. Spellmeyer and R. Wheeler (Elsevier, 2007), Vol. 3, pp. 155–176.
- [73] T. Furtenbacher, A. G. Császár, and J. Tennyson, MARVEL: Measured active rotational–vibrational energy levels, *J. Mol. Spectrosc.* **245**, 115 (2007).
- [74] T. Furtenbacher and A. G. Császár, MARVEL: Measured active rotational–vibrational energy levels. II. Algorithmic improvements, *J. Quant. Spectrosc. Radiat. Transf.* **113**, 929 (2012).
- [75] A. G. Császár and T. Furtenbacher, Spectroscopic networks, *J. Mol. Spectrosc.* **266**, 99 (2011).
- [76] T. Furtenbacher and A. G. Császár, The role of intensities in determining characteristics of spectroscopic networks, *J. Mol. Struct.* **1009**, 123 (2012).
- [77] P. Árendás, T. Furtenbacher, and A. G. Császár, On spectra of spectra, *J. Math. Chem.* **54**, 806 (2016).
- [78] P. F. Bernath, MoLLIST: Molecular line lists, intensities and spectra, *J. Quant. Spectrosc. Radiat. Transf.* **240**, 106687 (2020).