Radiative Transition Probabilities and Lifetimes for the Band Systems $A^2\Pi - X^2\Sigma^+$ of the Isovalent Molecules BeF, MgF and CaF

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Accurate potential energy curves, transition moments, spectroscopic constants, radiative transition probabilities, and lifetimes for the states $X^2\Sigma^+$ and $A^2\Pi$ of BeF, MgF and CaF are reported using high level calculations. Diagonal transitions dominate for the $A^2\Pi \rightarrow X^2\Sigma^+$ system. Radiative lifetimes for $v' = 0$ are predicted to be 6.81 ns, 7.16 ns and 19.48 ns, respectively for BeF, MgF and CaF. The result calculated for the CaF molecule are in excellent agreement with the experimental result equal to 21.9 ± 4.0 ns.

I. INTRODUCTION

The characterization of the electronic ground state ($X^2\Sigma^+$) and the first excited state ($A^2\Pi$) of the molecules BeF, MgF and CaF has been well established both experimentally [1–5] and theoretically [6–15]. Despite of the existence of various theoretical investigations on theses molecules [6–15], as far as we know, there is not any study reporting results for transition probabilities and radiative lifetimes for the MgF similar to that carried out for BeF [11]. However, for the CaF molecule, the radiative lifetime for $v' = 0$ of the $A^2\Pi \rightarrow X^2\Sigma^+$ transitions was determined equal to 21.9 ± 4.0 ns directly from the rate of fluorescence decay using a pulsed dye laser as an excitation source [16]. Recently, we have also concluded similar studies for the diatomic molecules formed by the alkaline-earth atoms (Be, Mg and Ca) with the second period atoms (B, C and N) [17–19].

With the purpose of providing additional results that can contribute to future spectral analysis and spectroscopic characterization of these molecules, the present study, by focusing mainly on the two doublet electronic states $X^2\Sigma^+$ and $A^2\Pi$, provides a unique comparative study of the spectroscopic properties of these isovalent alkaline-earth monofluorides. Using the same theoretical approach for the three systems, namely multireference singles and doubles configuration interaction (MRCI) and moderately large basis sets, a comparative characterization of their emission processes via the calculation of radiative transition probabilities and the radiative lifetimes of the band systems $A^2\Pi - X^2\Sigma^+$ is presented. It is expected that these results can complement and guide further experimental work on these systems.

II. METHODS

In this work we are concerned with a description of the first two lower-lying states ($X^2\Sigma^+$ and $A^2\Pi$) of the BeF, MgF and CaF molecules. Both states are correlated with the first lowest dissociation channel (M (^1S_g) + F (^2P_u); M = Be, Mg, Ca). The electronic calculations basically involved two steps. In the first one, the aim was to assess the importance of static correlation effects and to define a common set of molecular orbitals; in the second step, one was mainly concerned with incorporating as much dynamic correlation as possible in the final wavefunction having in mind a balance between its dimension and computation time. Our choice of atomic basis functions was the augmented correlation-consistent polarized valence quadruple-zeta (aug-cc-pVQZ) type developed by Dunning and collaborators available at the Extensible Computational Chemistry Environment Basis Set Database [20–22].

For each molecule, the first step consisted of state-averaged complete active space self-consistent field (CASSCF) [23, 24] calculations for three doublet states. At C_{2v} point group, the three doublet states are distributed according to the symmetry representations $A_1(1)$, $B_1(1)$, $B_2(1)$. Averaged natural orbitals were computed using the CASSCF wavefunctions which contained all possible electronic excitations resulting from the distribution of 9 electrons into 8 active orbitals (4,2,2,0), which comprised the valence orbitals. The final multireference configuration interaction wavefunction (MRCI) was generated as all single and double excitations from the reference set formed by all the CASSCF configurations. The MRCI wavefunction was constructed by the internally contracted approach [25, 26] implemented in the MOLPRO suite of programs [27]. Using the MRCI wavefunctions we have generated potential energy functions, dipole moment functions and transition moment functions.

The solution of Schrödinger's radial equation for the nuclear motion was carried out using the Intensity Program [28], which besides calculating vibrational-rotational energies and vibrational wavefunctions, allowed also for the calculation of radiative transition probabilities and radiative lifetimes.

Transition probabilities for emission as given by the Einstein $A_{v'v''}$ coefficients have been obtained by the expression

$$A_{v'v''} = 7.2356 \times 10^{-6} \, |< v' \, | \, \mu_{T_M}(R) \, | \, v'' >|^2 \, v_{v'v''}^3 \, \frac{(2-\delta_{0,\Lambda'+\Lambda''})}{(2-\delta_{0,\Lambda'})} \tag{1}$$

where $\mu_{T_M}(R)$ is the electronic transition moment function, $< v' \,|$ and $|\, v'' >$ symbolize the upper and lower vibrational state wavefunctions, $v_{v'v''}$ is the transition energy, and $\frac{(2-\delta_{0,\Lambda'+\Lambda''})}{(2-\delta_{0,\Lambda'})}$ is the degeneracy factor. The multiplication constant is the appropriate factor to express the probabilities in s^{-1}, when the transition moment is given in units of eÅ, and the energy in cm^{-1}. Radiative lifetimes were evaluated as the inverse of the total Einstein $A_{v'}$ coefficients. Spectroscopic constants were evaluated by standard fitting procedures [29].

III.   RESULTS AND DISCUSSION

In Figs. 1 to 3 are plotted the potential energy curves for the two lowest-lying states ($X^2\Sigma^+$ and $A^2\Pi$) of the isovalent molecules BeF, MgF and CaF, respectively. In Table I are summarized some spectroscopic constants for the three molecules calculated for the two electronic states along with previous experimental and theoretical results.
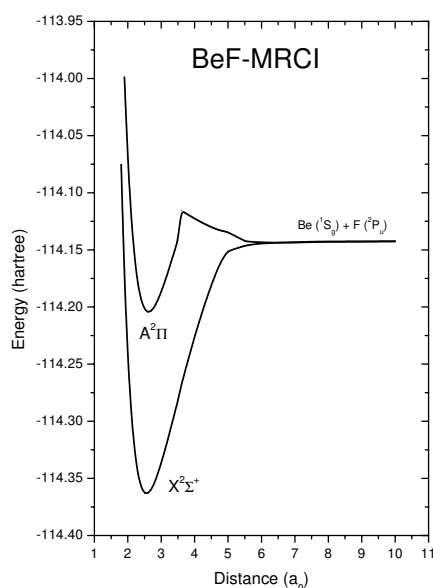

FIG. 1: Potential energy curves for the states $X^2\Sigma^+$ and $A^2\Pi$ of the BeF molecule.

In all molecules, as already described in a previous work for the BeF molecule [11], the ground state ($X^2\Sigma^+$) and the first excited state ($A^2\Pi$), around their equilibrium distances, are dominated, respectively, by the configurations $...n_{-1}\sigma^2 n\sigma^1 m\pi^4$ and $...n_{-1}\sigma^2 m\pi^4 m_{+1}\pi^1$ with the coefficient squared of these CSF (c^2) greater than 0.90. The orbitals $n_{-1}\sigma$ and $m\pi$ correspond essentially to the 2p orbital of the fluorine
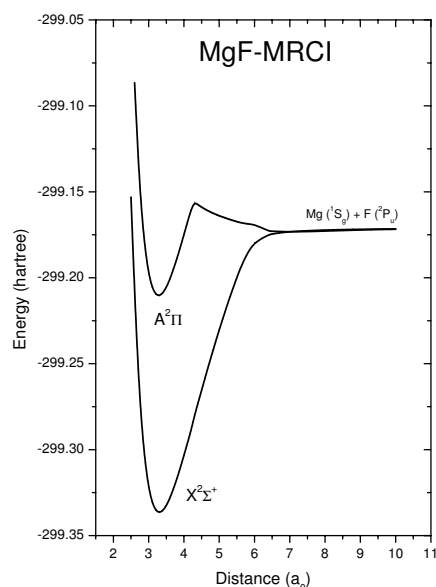

FIG. 2: Potential energy curves for the states $X^2\Sigma^+$ and $A^2\Pi$ of the MgF molecule.

atom and the $n\sigma$ and $m_{+1}\pi$ molecular orbitals correspond to the 2s and 2p orbitals of the alkaline-earth atom. These configurations describe an ionic structure with the polarity M^+F^-. At large distances the configurations change to properly describe a covalent structure at the dissociation limit M (^1S_g) + F (^2P_u).

The equilibrium distances for the states $X^2\Sigma^+$ and $A^2\Pi$ increase as the size of the metallic atom increases, similarly to the trend in the equilibrium distances for the first two electronic states of the alkaline-earth monoborides BeB, MgB and CaB [17], and alkaline-earth monocarbides BeC, MgC and CaC [19]. For both states of all molecules, our R_e results are slightly shorter than previous theoretical studies, thus improving the agreement with experiment. For the adiabatic excitation energy (T_e), our results for BeF, MgF and CaF are respectively equal to 34902, 27674 and 16421 cm^{-1}. If reference is made to the experimental T_e values, respectively equal to 33233.7, 27816.1 and 16489.8 cm^{-1} [1], the present results provide a more accurate characterization than those estimated by previous theoretical results 35085, 28955 and 17712 cm^{-1}, respectively [10, 14]. The spectroscopic constants ω_e and $\omega_e\chi_e$ usually depend on the number of spacings and on the number of adjustable parameters. Our values were calculated with nine spacings and two parameters show an overall good agreement with previous studies. These results can somehow be used to assess the quality of the overall description of the present calculations.

TABLE I: Energies at equilibrium distances (hartrees), equilibrium distances (a_0), spectroscopic vibrational constants (cm^{-1}), and electronic terms (cm^{-1}) for the two doublet states of BeF, MgF and CaF.

	BeF		MgF		CaF	
	$X^2\Sigma^+$	$A^2\Pi$	$X^2\Sigma^+$	$A^2\Pi$	$X^2\Sigma^+$	$A^2\Pi$
$-E_e^a$	0.36370	0.20467	0.33668	0.21059	0.48519	0.41037
R_e	2.557	2.617	3.300	3.280	3.725	3.692
	2.587^b	2.636^b	3.307^d	3.301^d	3.717^d	3.689^d
	2.587^c	2.621^c	3.310^e		3.733^g	3.699^g
	2.572^d	2.633^d	3.307^f		3.688^h	3.661^h
ω_e	1339.3	1226.8	774.6	790.4	612.5	624.0
	1272.5^b	1175.4^b	711.7^d	746.0^d	581.1^d	586.8^d
	1258^c	1184^c			581.2^g	579.9^g
	1247.4^d	1154.7^d				
$\omega_e\chi_e$	8.34	7.42	3.81	4.00	3.70	3.77
	9.52^b	8.80^b				
	8.80^c	13.5^c				
T_e	0	34902	0	27674	0	16421
		35085^e		28955^e		16489.8^d
		33233.7^d		27816.1^d		17712^g
						16526.8^h

^{a}The energy at the equilibrium distance for BeF is given relative to -114.0 a.u.; for MgF relative to -229.0 a.u.; and for CaF
relative to -776.0 a.u..
^{b}MRSDCI from Ref.[11]. ^{c}MRCI from Ref.[6].
^{d}Exp. from Ref.[1]. ^{e}MRCI from Ref.[14].
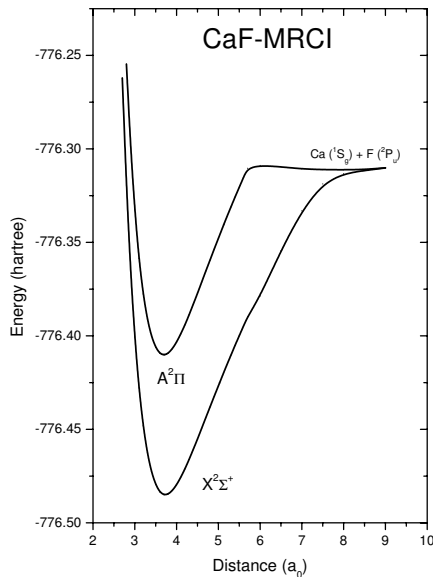^{f}Exp. from Ref.[4]. ^{g}MRCI from Ref.[10]. ^{h}Exp. from Ref.[6].

FIG. 3: Potential energy curves for the states $X^2\Sigma^+$ and $A^2\Pi$ of the CaF molecule.

The dipole and transition moments as a function of the internuclear distance are plotted in Figs. 4 to 6 for the three molecules. Negative values of the dipole moment correspond to the polarity M^+F^- . As already obtained for the BeF molecule [11], the dipole moments, for both states in all molecules, take on negatively increasing values until they reach a region where the configurations describing these states change character significantly to properly describe the dissociation, as discussed before. At large distances the dipole moments go to zero reflecting the dissociation into neutral species. The transition moment functions initially show a linear behavior and then undergoes an abrupt change in the regions where the $A^2\Pi$ state changes its character due to an avoided crossing with a higher-lying excited state, and then go asymptotically to zero as expected, because the two states dissociate into the same channel. For BeF, our dipole and transition moment functions are similar to those calculated in previous work [11]; for the MgF and CaF molecules, as far as we know, no previous dipole and transition moments have been reported.

Transition probabilities for emission as given by the Einstein $A_{v'v''}$ coefficients, and Franck-Condon factors ($q_{v'v''}$) for the $A^2\Pi \rightarrow X^2\Sigma^+$ band system are presented in Tables II to IV, respectively for the molecules BeF, MgF, and CaF. For all molecules, since the equilibrium internuclear distances for both states are close, and the potential energy curves are similar, predictions based on the Franck-Condon principle are expected to agree with those derived from the emission coefficients, i.e. strong diagonal transitions ($\Delta v = 0$) will occur predominantly. Total transition probabilities ($A_{v'}$) and radiative lifetimes are listed in the bottom section of Tables II to IV together with a check on the Franck-Condon sum rule ($\sum_{v''}q_{v'v''} = 1$). For the BeF molecule, the present lifetimes differ by approximately a factor of one-half from our previous work [11] due to a different convention used in the computation of the transition probabilities. The calculated radiative lifetimes for $v' = 0$ are equal to 6.81 ns, 7.16 ns, and 19.48

TABLE II: Einstein coefficients $A_{v'v''}$ (s^{-1}), Franck-Condon factors (second lines), total Einstein $A_{v'}$ coefficients (s^{-1}), and radiative lifetime (ns) of various vibrational levels for the $A^2\Pi$ - $X^2\Sigma^+$ band systems of BeF

v''	$v'=0$	$v'=1$	$v'=2$	$v'=3$	$v'=4$	$v'=5$
0	1.324×10^8	1.934×10^7	1.868×10^6	1.552×10^5	1.397×10^4	1.709×10^3
	0.882	0.109	0.009	0.001	0.000	0.000
1	1.395×10^7	9.858×10^7	3.354×10^7	5.275×10^6	6.280×10^5	7.122×10^4
	0.113	0.667	0.192	0.026	0.002	0.000
2	5.735×10^5	2.541×10^7	7.068×10^7	4.232×10^7	9.562×10^6	1.509×10^6
	0.005	0.208	0.486	0.246	0.047	0.006
3	1.088×10^4	1.616×10^6	3.402×10^7	4.863×10^7	4.684×10^7	1.413×10^7
	0.000	0.016	0.282	0.339	0.277	0.072
4	8.929×10^0	3.985×10^4	3.019×10^6	4.012×10^7	3.154×10^7	4.807×10^7
	0.000	0.000	0.030	0.337	0.224	0.289
5	1.836×10^{-1}	9.547×10^1	9.486×10^4	4.777×10^6	4.394×10^7	1.883×10^7
	0.000	0.000	0.001	0.049	0.375	0.136
6	8.103×10^{-1}	3.377×10^{-1}	6.101×10^2	1.869×10^5	6.824×10^6	4.569×10^7
	0.000	0.000	0.000	0.002	0.071	0.395
7	5.612×10^{-4}	7.405×10^0	4.412×10^2	2.083×10^3	3.250×10^5	9.064×10^6
	0.000	0.000	0.000	0.000	0.004	0.095
8	4.202×10^{-3}	6.604×10^{-1}	1.419×10^1	1.218×10^1	4.987×10^3	5.117×10^5
	0.000	0.000	0.000	0.000	0.000	0.007
9	3.506×10^{-2}	2.253×10^{-2}	3.199×10^0	1.601×10^1	1.575×10^1	9.317×10^3
	0.000	0.000	0.000	0.000	0.000	0.000
10	2.017×10^{-3}	2.694×10^{-3}	4.382×10^{-2}	7.959×10^0	9.955×10^0	1.312×10^1
	0.000	0.000	0.000	0.000	0.000	0.000
$^aA_{v'}$	1.469×10^8	1.450×10^8	1.432×10^8	1.415×10^8	1.397×10^8	1.379×10^8
$^aQ_{v'}$	1.000	1.000	1.000	1.000	1.000	1.000
$\tau_{v'}$	6.81	6.90	6.98	7.07	7.16	7.25

$$^aQ_{v'} = \Sigma_{v''=0}^{10} q_{v'v''} \text{ and } A_{v'} = \Sigma_{v''=0}^{10} A_{v'v''}$$
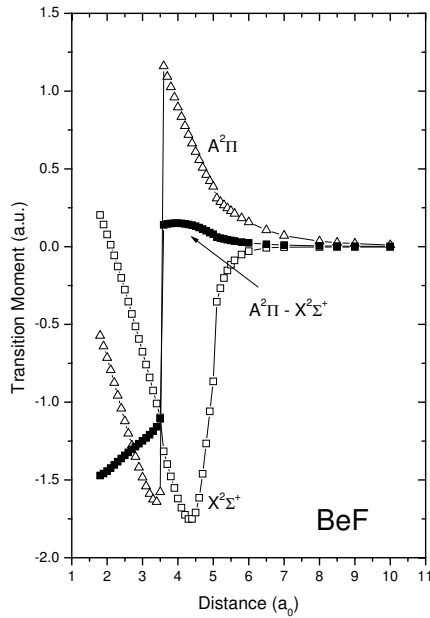

FIG. 4: Transition moment and dipole moment functions for the states $X^2\Sigma^+$ and $A^2\Pi$ of the BeF molecule.
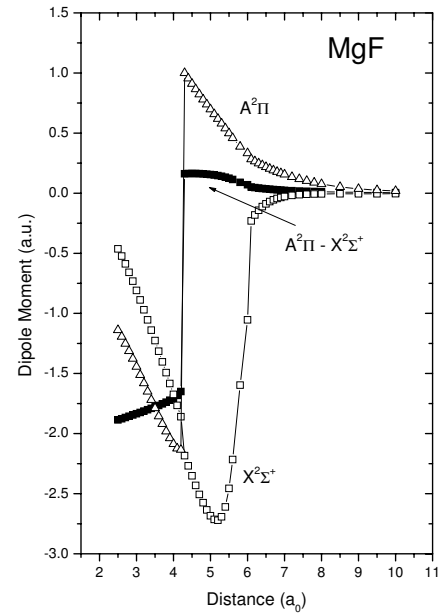
FIG. 5: Transition moment and dipole moment functions for the states $X^2\Sigma^+$ and $A^2\Pi$ of the MgF molecule.

TABLE III: Einstein coefficients $A_{v'v''}$ (s^{-1}), Franck-Condon factors (second lines), total Einstein $A_{v'}$ coefficients (s^{-1}), and radiative lifetime (ns) of various vibrational levels for the $A^2\Pi$ - $X^2\Sigma^+$ band systems of MgF

v''	$v'=0$	$v'=1$	$v'=2$	$v'=3$	$v'=4$	$v'=5$
0	1.377×10^8	1.894×10^6	3.220×10^3	1.972×10^2	5.884×10^1	1.973×10^1
	0.986	0.014	0.000	0.000	0.000	0.000
1	1.902×10^6	1.340×10^8	3.536×10^6	2.322×10^3	6.087×10^2	4.642×10^1
	0.014	0.961	0.026	0.000	0.000	0.000
2	2.615×10^4	3.511×10^6	1.307×10^8	5.014×10^6	1.222×10^3	6.736×10^2
	0.000	0.025	0.938	0.037	0.000	0.000
3	1.550×10^2	9.108×10^4	4.897×10^6	1.275×10^8	6.496×10^6	1.812×10^3
	0.000	0.000	0.035	0.917	0.048	0.001
4	2.068×10^1	1.357×10^3	1.870×10^5	6.244×10^6	1.241×10^8	8.153×10^6
	0.000	0.000	0.001	0.044	0.894	0.060
5	1.732×10^1	4.916×10^1	5.322×10^3	2.986×10^5	7.732×10^6	1.204×10^8
	0.000	0.000	0.000	0.003	0.055	0.869
6	1.916×10^0	5.006×10^1	9.506×10^1	1.403×10^4	4.247×10^5	9.348×10^6
	0.000	0.000	0.000	0.000	0.003	0.066
7	1.287×10^{-2}	9.738×10^0	7.572×10^1	3.081×10^2	2.756×10^4	5.716×10^5
	0.000	0.000	0.000	0.000	0.000	0.004
8	1.043×10^{-1}	3.176×10^{-4}	3.600×10^1	7.677×10^1	9.998×10^2	4.444×10^4
	0.000	0.000	0.000	0.000	0.000	0.000
9	2.822×10^{-2}	2.285×10^{-1}	7.948×10^{-1}	7.246×10^1	7.689×10^1	2.510×10^3
	0.000	0.000	0.000	0.000	0.000	0.000
10	8.160×10^{-6}	1.500×10^{-2}	6.800×10^{-1}	6.812×10^0	9.484×10^1	1.049×10^2
	0.000	0.000	0.000	0.000	0.000	0.000
${}^a A_{v'}$	1.396×10^8	1.395×10^8	1.393×10^8	1.390×10^8	1.388×10^8	1.385×10^8
${}^a Q_{v'}$	1.000	1.000	1.000	1.000	1.000	1.000
$\tau_{v'}$	7.16	7.17	7.18	7.19	7.21	7.22

$${}^a Q_{v'} = \Sigma_{v''=0}^{10} q_{v'v''} \text{ and } A_{v'} = \Sigma_{v''=0}^{10} A_{v'v''}$$
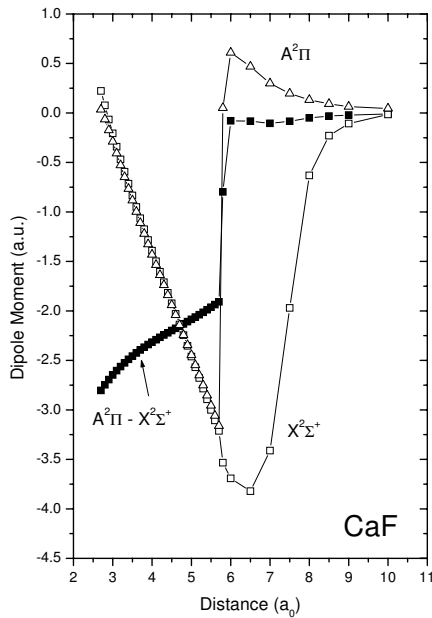

FIG. 6: Transition moment and dipole moment functions for the states $X^2\Sigma^+$ and $A^2\Pi$ of the CaF molecule.

ns for BeF, MgF and CaF, respectively. Compared with the only known experimental result (for the CaF molecule), equal to 21.9 ± 4.0 ns [16], our prediction turns out to be very good.

IV. CONCLUSIONS

The present work reports a comparative high-level theoretical characterization of spectroscopic properties and electronic transitions of the two lowest-lying doublet electronic states ($X^2\Sigma^+$ and $A^2\Pi$) of the isovalent molecules BeF, MgF, and CaF. For MgF, in particular, radiative transition probabilities and lifetimes are reported for the first time. For all molecules, the most intense transitions are predicted to be those of the (0,0) band of the $A^2\Pi \rightarrow X^2\Sigma^+$ system; other diagonal transitions are also expected to be strong. Radiative lifetimes for $v' = 0$ are predicted to be 6.81 ns, 7.16 ns, and 19.48 ns, respectively for BeF, MgF, and CaF. The value for the CaF molecule is in excellent agreement with the experimental result of 21.9 ± 4.0 ns [16]. For the other two molecules, due to the similarity of the theoretical approaches, we are confident that the present results can faithfully be used by in future investigations of these molecules.

TABLE IV: Einstein coefficients $A_{v'v''}$ (s^{-1}), Franck-Condon factors (second lines), total Einstein $A_{v'}$ coefficients (s^{-1}), and radiative lifetime (ns) of various vibrational levels for the $A^2\Pi$ - $X^2\Sigma^+$ band systems of CaF

v''	$v'= 0$	$v'= 1$	$v'= 2$	$v'= 3$	$v'= 4$	$v'= 5$
0	4.950×10^7	1.842×10^6	9.902×10^3	1.001×10^2	4.681×10^0	4.730×10^0
	0.964	0.036	0.000	0.000	0.000	0.000
1	1.767×10^6	4.592×10^7	3.562×10^6	2.596×10^4	2.383×10^2	7.756×10^0
	0.035	0.895	0.070	0.000	0.000	0.000
2	6.437×10^4	3.315×10^6	4.251×10^7	5.238×10^6	4.959×10^4	2.104×10^2
	0.001	0.065	0.830	0.103	0.001	0.000
3	2.024×10^3	1.907×10^5	4.708×10^6	3.918×10^7	6.914×10^6	8.360×10^4
	0.000	0.004	0.092	0.767	0.136	0.002
4	6.189×10^1	9.157×10^3	3.726×10^5	5.987×10^6	3.593×10^7	8.540×10^6
	0.000	0.000	0.008	0.117	0.704	0.168
5	5.745×10^0	4.049×10^2	2.511×10^4	6.000×10^5	7.122×10^6	3.289×10^7
	0.000	0.000	0.000	0.012	0.139	0.646
6	1.490×10^0	4.279×10^1	1.506×10^3	5.167×10^4	8.613×10^5	8.075×10^6
	0.000	0.000	0.000	0.001	0.018	0.158
7	3.899×10^{-1}	1.114×10^1	1.440×10^2	3.903×10^3	8.819×10^4	1.138×10^6
	0.000	0.000	0.000	0.000	0.002	0.023
8	8.139×10^{-2}	1.933×10^0	3.104×10^1	3.422×10^2	7.810×10^3	1.338×10^5
	0.000	0.000	0.000	0.000	0.000	0.003
9	2.611×10^{-3}	8.519×10^{-2}	4.680×10^0	5.231×10^1	6.832×10^2	1.352×10^4
	0.000	0.000	0.000	0.000	0.000	0.000
10	9.644×10^{-3}	2.172×10^{-2}	7.484×10^{-3}	7.214×10^0	8.249×10^1	1.255×10^3
	0.000	0.000	0.000	0.000	0.000	0.000
$^aA_{v'}$	5.133×10^7	5.127×10^7	5.119×10^7	5.108×10^7	5.098×10^7	5.088×10^7
$^aQ_{v'}$	1.000	1.000	1.000	1.000	1.000	1.000
$\tau_{v'}$	19.48	19.50	19.54	19.58	19.62	19.65

$$^aQ_{v'} = \Sigma_{v''=0}^{10} q_{v'v''} \text{ and } A_{v'} = \Sigma_{v''=0}^{10} A_{v'v''}$$

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