Theoretical study of the UV photodissociation of Cl\textsubscript{2}: Potentials, transition moments, extinction coefficients, and Cl\textsuperscript{\#}/Cl branching ratio

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Potential energy curves for the $X^1\Sigma^+_g$ ground state and $\Omega=0^+_u$, $1_u$ valence states and dipole moments for the $0^+_u$, $1_u$–$X$ transitions are obtained in an \textit{ab initio} configuration interaction study of Cl\textsubscript{2} including spin-orbit coupling. In contrast to common assumptions, it is found that the $B^3\Pi_{0^+_u}$–$X$ transition moment strongly depends on internuclear distance, which has an important influence on the Cl\textsubscript{2} photodissociation. Computed energy curves and transition moments are employed to calculate the $A$, $B$, $C$–$X$ extinction coefficients, the total spectrum for the first absorption band, and the Cl\textsuperscript{\#}($2\,P_{3/2}$)/Cl($2\,P_{3/2}$) branching ratio as a function of excitation wavelength. The calculated data are shown to be in good agreement with available experimental results. © 2004 American Institute of Physics. [DOI: 10.1063/1.1753554]

I. INTRODUCTION

The chlorine molecule is widely used as a benchmark system for studying the electronic structure and photodissociation dynamics of diatomics under various conditions: in gas phase,\textsuperscript{1–12} in rare gas matrices,\textsuperscript{13} or as an adsorbate.\textsuperscript{14} The well-known first absorption band of the Cl\textsubscript{2} molecule is located in the UV region with a maximum at 330 nm and corresponds to the Cl\textsubscript{2} excitation to the valence states correlating with the Cl($2\,P_{1/2,3/2}$) atomic products. This absorption spectrum has been thoroughly studied experimentally in the last few decades and is attributed mainly to the transition to the lowest repulsive $C^1\Pi_{1_u}$ state.\textsuperscript{1,7–9,15} There are also small admixtures of the $A^3\Pi_{1_u}$–$X$ and $B^3\Pi_{0^+_u}$–$X$ continuum bands in the long wavelength part of the spectrum which are unresolved and appear as a shoulder on the low-energy wing of the main $C$–$X$ peak. There are three possible Cl\textsubscript{2} dissociation channels corresponding to combinations of the two Cl atoms in their ground Cl($2\,P_{3/2}$) and spin-excited Cl\textsuperscript{\#}($2\,P_{1/2}$) states. The $C$ and $A$ states correlate with the ground state chlorine atoms in the adiabatic approximation, whereas the $B$ state gives Cl+Cl\textsuperscript{\#} upon dissociation.

Two types of nonadiabatic transitions can influence the photodissociation process: a heterogeneous transition ($\Delta\Omega=1$) between $C^1\Pi_{1_u}$ and $B^3\Pi_{0^+_u}$ states which cross one another on their way to dissociation, and homogeneous transitions ($\Delta\Omega=0$) between the $1_u$ valence states. A series of experimental studies has been carried out to determine the dissociation channels and role of nonadiabatic effects in the Cl\textsubscript{2} photodissociation.\textsuperscript{2–5,10–12} It has been shown that the probability of heterogeneous transitions between the $C$ and $B$ states is negligibly small.\textsuperscript{6,10} On the contrary, the homogeneous nonadiabatic processes have been found to be very important, in particular in the 300–350 nm excitation range, leading to an increase in the Cl\textsuperscript{\#} yield upon dissociation due to transitions from the $C$ state to the higher-lying $1_u$ states correlating with Cl+Cl\textsuperscript{\#}.\textsuperscript{2,3,5,6,16}

In spite of extensive investigations of the Cl\textsubscript{2} first absorption system, information about the potential energy curves and transition moments for the relevant excited states is far from being complete and unambiguous. The first \textit{ab initio} potential curves for the Cl\textsubscript{2} molecule were computed by Peyerimhoff and Buenker\textsuperscript{16} in the $\Lambda$–$S$ approximation and served for many years after as a theoretical basis for analysis of the experimental data. \textit{Ab initio} calculations including spin-orbit coupling have been performed only recently\textsuperscript{6} for the valence states involved in the dissociation process. In this study, transition dipole moments have been reported only for the $R_s(X)$ equilibrium distance of the ground state. Moreover, the dipole moment of the dominant $C$–$X$ transition obtained in Ref. 6 at $R_s(X)$ is 30% lower than that derived from the experimental data.\textsuperscript{17,18} It can be noted that the $C$–$X$ transition is by far the strongest one of the first absorption system, which significantly facilitates its experimental analysis and makes data obtained so far for the $C$ state the most consistent and reliable. The potential energy curve of the $C$ state in the Franck–Condon region has been derived from the Raman spectra of Cl\textsubscript{2}.\textsuperscript{19,20} In addition, the $C$–$X$ transition moment has been calculated by employing the time-dependent Hartree–Fock method and the second-order polarization propagator approximation (both methods have been used in Ref. 19) and found to be $\sim 10\%$ smaller than the experimental values\textsuperscript{17,18} at the ground state equilibrium distance.

Experimental information on the $B$–$X$ absorption band is quite uncertain, since it is significantly overlapped by the more intense $C$–$X$ band as well as the weaker $A$–$X$ one. The vertical excitation energy of the $B$ state, estimated from the total absorption spectrum, varies by several thousand wave numbers in different studies\textsuperscript{2,15,18} and the squared $B$–$X$ transition moment values determined in Refs. 15 and 18 differ by a factor of 2. More reliable data for the $B$–$X$ tran-
sition moment have been obtained from the lifetime measurements carried out for the \( B, \upsilon'' = 7 - 12 \) vibrational levels.\(^{21,22}\) The range of internuclear distance for which the dipole moment can be obtained from these data is out of the Franck–Condor region of the \( X, \upsilon'' = 0 \) state, however.

The \( A \) state is even more complicated to describe with high precision based on the first absorption band data because the \( A \rightarrow X \) transition is very weak. Several estimates of the vertical excitation energy and dipole moment based on comparison with the \( C \rightarrow X \) band intensity have been made employing the Cl atom spin-orbit constant,\(^{15,18}\) and they differ significantly from one another. In addition, the \( A \rightarrow X \) dipole moment for low vibrational levels of the \( A \) state has been derived from the ratio between the \( A \rightarrow X \) and \( B \rightarrow X \) emission line intensities.\(^{23,24}\)

From the above discussion it is clear that in order to achieve a reliable theoretical description of the \( \text{Cl}_2 \) photodissociation in its first absorption band, it is necessary to significantly improve the accuracy of the calculated data for the photoabsorption process. This information is also very important for the analysis of nonadiabatic processes and experimental data on the photodissociation. The goal of the present work is to carry out extensive configuration interaction (CI) calculations including spin-orbit coupling for potential energy curves of the \( X^1 \Sigma_g^+ \), \( \Omega_u \), and \( \Lambda_u \) valence states of \( \text{Cl}_2 \) and the corresponding transition dipole moments over a large interval of internuclear distance. Special attention is paid to the accuracy of the transition moment calculations for the first absorption band states of \( \text{Cl}_2 \). We have not included valence states with other \( \Omega \) values (\( \Omega = 0, 2, \) and 3) in this study, since they are not relevant to the photodissociation process discussed. A theoretical description of these states can be found in our previous work.\(^{25}\)

The computed potential curves and transition moments are employed to analyze the direct photoexcitation process, in particular, to calculate the corresponding extinction coefficients and the \( \text{Cl}^* / \text{Cl} \) branching ratio as functions of excitation wavelength, and to compare them with available experimental data.

### II. COMPUTATIONAL DETAILS

A detailed description of the theoretical approach for calculation of the potential energy curves and transition dipole moments for the \( \text{Cl}_2 \) molecule may be found in our previous study.\(^{25}\) Briefly, the \( \Lambda \rightarrow \Sigma \) potential curves have been calculated by employing the multireference singles and doubles (MRD-CI) method\(^{26}\) in combination with relativistic effective core potentials (RECPs)\(^{27}\) used for description of the core electrons (\( 1 \text{s}^2 \text{2s}^2 \text{2p}^6 \)) of the chlorine atoms. The RECP spin-orbit (SO) operator has been scaled with a factor of 1.04 to achieve better agreement with experimental SO splittings for the neutral Cl atom and its cation (see Ref. 25). The \( \text{Cl}( \Sigma^\text{g}_u) \) ground state splitting calculated with thus optimized SO operator has been found to be 878 cm\(^{-1}\), in very good agreement with the experimental value of 881 cm\(^{-1}\). An atomic Gaussian basis set employed has been changed with respect to that of the previous work:\(^{25}\) three \( d \) and two \( f \) polarization functions with the exponents from Ref. 28 as well as one \( s \) and one \( p \) diffuse functions (exponents of 0.0608 and 0.0466, respectively) have been added to the valence set of Ref. 27, giving altogether a \( \text{7s6p3d}2f \) basis.

All 12 \( \Lambda \rightarrow \Sigma \) states correlating with the \( \text{Cl}(2\Sigma)^+ + \text{Cl}(2\Pi) \) dissociation limit and the lowest \( \Sigma^+_u \) ion-pair/Rydberg state have been included in the calculations (potentials for all low-lying valence and Rydberg \( \Lambda \rightarrow \Sigma \) states can be found in Figs. 1 and 2 of Ref. 25). The CI procedure has been carried out at a configuration selection threshold of \( T = 0.02 \mu \text{E}_h \), with the subsequent energy extrapolation to \( T = 0.26 \). In addition, some points have been computed at the lower thresholds, \( T = 0.01 \) and \( T = 0.005 \mu \text{E}_h \), to attain better accuracy for the transition moments. Finally, the multireference analog of the Davidson correction\(^{29}\) has been in-

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**TABLE I. Technical details of the MRD-CI calculations at various selection thresholds**

<table>
<thead>
<tr>
<th>( D_{2h} )</th>
<th>( N_{\text{root}} )</th>
<th>( N_{\text{ref}} )</th>
<th>SAFSEL</th>
<th>( T = 0.05 )</th>
<th>( T = 0.02 )</th>
<th>( T = 0.01 )</th>
<th>( T = 0.005 )</th>
<th>( D_{\text{nh}} )</th>
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<tr>
<td>( ^1A_g )</td>
<td>1</td>
<td>101</td>
<td>11 443 562</td>
<td>249 221</td>
<td>405 772</td>
<td>620 077</td>
<td>( 1 ) ( ^1 \Sigma^+_u )</td>
<td>( 1 ) ( ^1 \Delta_u )</td>
</tr>
<tr>
<td>( ^3B_{2u} )</td>
<td>1</td>
<td>86</td>
<td>16 979 548</td>
<td>141 559</td>
<td>244 990</td>
<td>393 655</td>
<td>647 393</td>
<td>( 2 ) ( ^1 \Sigma^+_u )</td>
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<tr>
<td>( ^1B_{1g} )</td>
<td>1</td>
<td>85</td>
<td>19 321 843</td>
<td>194 434</td>
<td>309 697</td>
<td>458 687</td>
<td>( 1 ) ( ^1 \Delta_u )</td>
<td></td>
</tr>
<tr>
<td>( ^1A_u )</td>
<td>1</td>
<td>79</td>
<td>11 560 152</td>
<td>170 772</td>
<td>300 351</td>
<td>469 215</td>
<td>( 1 ) ( ^1 \Delta_u )</td>
<td>( 2 ) ( ^1 \Sigma^+_u )</td>
</tr>
<tr>
<td>( ^3B_{2u} )</td>
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<td>54</td>
<td>11 588 336</td>
<td>159 586</td>
<td>257 132</td>
<td>377 395</td>
<td>( 1 ) ( ^1 \Pi_u )</td>
<td></td>
</tr>
<tr>
<td>( ^1A_u )</td>
<td>1</td>
<td>94</td>
<td>20 176 311</td>
<td>207 514</td>
<td>311 529</td>
<td>440 359</td>
<td>( 1 ) ( ^1 \Sigma^+_u )</td>
<td>( 2 ) ( ^1 \Delta_u )</td>
</tr>
<tr>
<td>( ^3B_{3u} )</td>
<td>1</td>
<td>68</td>
<td>29 795 478</td>
<td>172 187</td>
<td>273 228</td>
<td>410 394</td>
<td>( 1 ) ( ^1 \Pi_u )</td>
<td></td>
</tr>
<tr>
<td>( ^3B_{1g} )</td>
<td>1</td>
<td>68</td>
<td>27 987 534</td>
<td>248 019</td>
<td>385 307</td>
<td>559 571</td>
<td>( 1 ) ( ^1 \Sigma^+_u )</td>
<td>( 2 ) ( ^1 \Delta_u )</td>
</tr>
<tr>
<td>( ^3B_{1u} )</td>
<td>1</td>
<td>80</td>
<td>29 623 217</td>
<td>428 588</td>
<td>635 203</td>
<td>880 123</td>
<td>( 1 ) ( ^1 \Sigma^+_u )</td>
<td></td>
</tr>
<tr>
<td>( ^1A_u )</td>
<td>1</td>
<td>71</td>
<td>34 028 692</td>
<td>281 023</td>
<td>421 661</td>
<td>571 293</td>
<td>( 1 ) ( ^1 \Delta_u )</td>
<td></td>
</tr>
</tbody>
</table>

*The numbers of selected symmetry adapted functions (SAFs) are given for \( r = 3.80 \text{a}_\text{u} \). SAFSEL designates the total number of generated, SAFSEL the number of selected SAFs, \( N_{\text{ref}} \) and \( N_{\text{root}} \) refer to the number of reference configurations and roots treated, respectively.*
Test calculations have also been carried out with one additional g basis function, but its influence on the computed potentials and transition moments in the Franck–Condon region has been found to be negligible and the corresponding data are not included in the paper. The computed potential curves have been smoothed with cubic spline and employed for numerical solution of the one-dimensional nuclear motion Schrödinger equation to obtain vibrational wave functions. The latter are combined with the \textit{ab initio} transition moments in order to compute extinction coefficients for various transitions of the first absorption band as well as the Cl$^\text{I}/\text{Cl}$ branching ratio as functions of internuclear distance.

### III. RESULTS AND DISCUSSION

#### A. Potential energy curves

There are six $\Omega$ valence states of Cl$_2$, which are connected with the ground state by the electric–dipole transitions: one state of the 0$^+_u$ symmetry ($B^1 \Pi_0^0 \Rightarrow u$) and five 1$^u$ states: $A^3 \Pi_1$, $C^1 \Pi_1$, $1_g(III, 1^3 \Sigma^+_u)$, $1_u (IV, 2^3 \Sigma^+_u)$, and $1_u (V, 3^3 \Delta_u)$. Their adiabatic potential energy curves are shown in Fig. 1. At small and intermediate internuclear distances, $R = 3.5$–$5.0 \, \text{a}_0$, each of the above $\Omega$ states is characterized by only one dominant $\Lambda$–$S$ component. At $R > 5.0 \, \text{a}_0$, the A state gains more 1$^1 \Pi_u$ character (7.5% at $R = 5.6 \, \text{a}_0$) and the C state has stronger 3$^3 \Pi_u$ and 1$^3 \Sigma^+_u$ contributions (5.4% and 8.9%, respectively, at $R = 5.6 \, \text{a}_0$). The 1$^3 \Pi_u$ (III) state becomes a mixture of the 3$^3 \Pi_u$–1$^3 \Sigma^+_u$ states, whereas 1$^1 \Pi_u (IV, 2^3 \Sigma^+_u)$ and 1$^1 \Pi_u (V, 3^3 \Delta_u)$ retain their $\Lambda$–$S$ character up to $R \sim 6.0 \, \text{a}_0$. The B state is almost pure 3$^3 \Pi_u$ over all $R$. The only notable admixture to this state comes from the 1$^3 \Sigma^+_u$–1$^3 \Sigma^+_u$ state around $R \approx 7.0 \, \text{a}_0$. Its weight in the resulting $B^0_u$ state does not exceed 0.1%, but it nonetheless gives an important contribution into the $B^1 \Omega$–$X^1 \Omega$ transition moment.

Spectroscopic constants for the $X, B$, and $A$ bound states obtained from the \textit{ab initio} potentials are given in Table II along with the experimental values. The computed and experimental data for the bound states are found to be in very

![FIG. 1. Computed adiabatic potential energy curves for the $X^1 \Sigma^+_u$ and $\Omega = 0^+_u, 1^u$ states correlating with two Cl(2$P_{3/2,1/2}$) atoms.](image)

### TABLE II. Spectroscopic constants calculated in the present study for the $^{35}\text{Cl} \, ^{35}\text{Cl}$ isotope at $T = 0.02 \, \mu E_\text{h}$ (no reference is given) in comparison with the experimental and previous theoretical data.

<table>
<thead>
<tr>
<th>State</th>
<th>$T_a / \text{cm}^{-1}$</th>
<th>$R_a / \text{Å}$</th>
<th>$D_a / \text{cm}^{-1}$</th>
<th>$\omega_a / \text{cm}^{-1}$</th>
<th>$\omega_a \lambda_a / \text{cm}^{-1}$</th>
<th>$\omega_a \lambda_a R_a / \text{cm}^{-1}$</th>
</tr>
</thead>
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<td>$X^1 \Sigma^+_u$</td>
<td>0</td>
<td>0</td>
<td>2.013</td>
<td>1.987</td>
<td>19400</td>
<td>549</td>
</tr>
<tr>
<td>$A^3 \Pi_1$</td>
<td>17</td>
<td>7</td>
<td>452</td>
<td>2.45</td>
<td>18833</td>
<td>265</td>
</tr>
<tr>
<td>$B^3 \Pi_0^0$</td>
<td>17</td>
<td>980</td>
<td>17</td>
<td>809</td>
<td>3210</td>
<td>259</td>
</tr>
<tr>
<td>$C^1 \Pi_1$</td>
<td>30</td>
<td>853</td>
<td>30</td>
<td>562</td>
<td>2912</td>
<td>240</td>
</tr>
</tbody>
</table>

$A$ vertical excitation energy is given for the $C$ state.

$\text{a}$Reference 1.

$\text{a}$Reference 30.

$\text{a}$Reference 6.

$\text{b}$Reference 24.

$\text{b}$Reference 32.

$\text{b}$Reference 17.

$\text{b}$Reference 18.
good agreement, as is the vertical excitation energy for the repulsive C state. One can note that the calculated \( R_e \) values are shifted to larger internuclear distances by 0.015–0.025 Å with respect to the corresponding experimental data. As can be concluded from the test calculations with various atomic basis sets and CI treatments of various dimensions, this effect is mainly a consequence of employing the effective core potential approach. Such systematic error depends relatively weakly on the concrete excited state and thus one can assume that all computed potential curves are shifted by approximately the same distance. Indeed, a parallel shift of the computed potential curves is shifted by approximately 0.025 Å leads to a very good agreement with the corresponding experimental curve in the Franck–Condon region. This is also true for the similarly shifted repulsive C state, which demonstrates good agreement with the experimental curves obtained from the Raman spectra simulation, as well as for the B state, where comparison with the experimentally derived potential is possible for \( R > 4.0 \) a.u. (see Fig. 2). Notable differences between computed and experimental potential curves are observed only outside the Franck–Condon region. One can therefore expect that the vertical excitation energies are reproduced in the present calculations quite accurately, which will be examined in more detail in the analysis of the absorption spectrum and the Cl/CI branching ratio.

The main deficiencies in the energy calculations appear at the intermediate and large internuclear distances and lead to an underestimation of the dissociation energies by \( \sim 700–900, \sim 520, \) and \( \sim 150 \) cm\(^{-1}\) for the X, A, and B states, respectively. This circumstance has no direct influence on the computed excitation spectra, however.

### B. Transition moment functions

#### 1. \( ^1\Pi_u \leftarrow X \Sigma^+ \)

Computed dipole moment functions for the \( 1_u \leftarrow 0_u^+ \leftarrow X \) transitions are shown in Fig. 3. The \( ^1\Pi_u \leftarrow X \Sigma^+ \) is the only spin-allowed transition in the first absorption band and thus clearly the strongest one since spin-orbit interaction is relatively weak in the CI\(_2\) molecule. Its dipole moment, \( \mu^{C-X} \), is almost completely determined by one dominant \( \Lambda-S \) contribution, \( ^1\Pi_u \leftarrow X \Sigma_g^+ \), in the whole range of internuclear distance. Our calculations show that the \( ^1\Pi_u \leftarrow X \Sigma_g^+ \) transition moment at the \( \Lambda-S \) level of treatment and hence the final \( \mu^{C-X} \) value depend strongly on the selection threshold employed in the MRD-CI selection procedure and thus on the completeness of the CI expansion. Results of the MRD-CI calculations of \( \mu^{C-X} \) at several thresholds are shown in Fig. 4(a). The magnitude of \( \mu^{C-X} \) increases noticeably with the decreasing threshold, from 0.267 D at \( T = 0.05 \mu E_h \) to 0.347 D at \( T = 0.005 \mu E_h \) (these results are obtained at \( R = R^X \), gradually approaching an experimental value of 0.356 D in Ref. 17).

#### 2. \( ^3\Pi_{0^+} \leftarrow X \Sigma^+ \)

The \( ^3\Pi_{0^+} \leftarrow X \Sigma_g^+ \) parallel transition becomes allowed only due to the spin-orbit interaction. It gets its intensity from two main contributions: \( ^3\Pi_u \leftarrow ^3\Pi_{g} \) and \( ^1\Sigma^+_u \leftarrow X \Sigma^+_g \). An admixture of \( ^3\Pi_u \) to the \( X \) state is quite small, but its value increases significantly with internuclear distances.
distance, from \( \approx 10^{-4} \) at \( R = 3.5 \alpha_0 \) up to 0.10 at \( R = 5.5 \alpha_0 \), which leads to a growth of the total \( B^3\Pi_{1/2} \rightarrow X^1\Sigma_g^+ \) transition moment in this distance range. The \( ^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+ \) transition is extremely strong and it is responsible for approximately \( 1/3 \) of the \( B-X \) value, in spite of the very small contribution of \( ^1\Sigma_u^+ \) to the \( B \) state. One should note that \( \mu_{B-X}(R) \) grows rapidly in the Franck–Condon region and varies only insignificantly in the \( 4.2–5.7 \alpha_0 \) interval, which is characteristic for the lowest vibrational levels of the \( B \) state. This behavior of the \( \mu_{B-X}(R) \) function has a strong influence on the shape of the \( B-X \) absorption spectrum in comparison with that obtained with the constant \( \mu_{B-X} \) value (see small panel in Fig. 5), whereas the \( B-X \) emission bands from the low \( B, v' \) vibrational levels may be fairly accurately treated with the constant transition moment.

There are several experimental values of the \( B-X \) transition moments derived from the \( B, v' = 7–12 \) lifetimes\(^{21,22} \) as well as from the absorption data.\(^{18} \) Based on the \( B, v' = 7–12 \) lifetimes, \( \mu_{B-X} \) can be obtained for the interval of \( R \approx 2.15–2.25 \) \( \AA \), since the corresponding Franck–Condon factors dominate the \( B-X \) emission. An experimental \( \mu_{B-X} \) value is determined to be 0.071 D (\( R = 2.15 \) \( \AA \))\(^{21–22} \) or 0.086 D (\( R = 2.15–2.25 \) \( \AA \))\(^{22} \) under assumption of its independence of \( R \) within the considered interval. In the \( \text{Cl}_2 \) chemiluminescence study,\(^{23} \) \( \mu_{B-X} \) has also been found to be constant in the \( R = 2.18–2.25 \) \( \AA \) interval. The \( \mu_{B-X} \) value computed in the present work at 2.1 \( \AA \) is 0.0696 D and thus agrees excel-

lently with the above experimental data. At larger bond lengths, \( \mu_{B-X} \) gradually increases, by \( \approx 7\% \) from 2.15 to 2.25 \( \AA \). It is therefore possible that the computed \( \mu_{B-X} \) value is slightly overestimated at \( R > 2.2 \) \( \AA \), but this discrepancy is within the experimental error bars. There is a relatively large discrepancy between \( \mu_{B-X} \) transition moments estimated from the absorption spectrum,\(^{18} \) 0.077 D, and computed at \( R_{c*}, 0.060 \) D. We think, however, that the value extracted from the experimental absorption spectrum is less reliable than that from the lifetime measurements for the reason given above. One should also note that in contrast to the perpendicular \( C-X \) transition, the dipole moment of the parallel \( B-X \) species does not change significantly with a CI selection threshold smaller than \( T = 0.05 \mu E_h \) [see Fig. 4(b)].

3. \( A^3\Pi_{1/2} \rightarrow X^1\Sigma_g^+ \)

The \( A^3\Pi_{1/2} \rightarrow X^1\Sigma_g^+ \) transition is also forbidden at the \( A-S \) level and mainly occurs due to the direct spin-orbit coupling between the \( 1^3\Pi_{1/2} \) and \( 1^1\Pi_1 \) states. Since both the \( A \) and \( C \) states converge to the CI(\( ^2P_{3/2}^0 \)) + CI(\( ^2P_{3/2} \)) atomic asymptote, the same as for the \( X^1\Sigma_g^+ \) ground state, the \( C, A \rightarrow X \) transition moments vanish at the dissociation limit. However, as the internuclear separation increases from \( R = 3.4 \alpha_0 \) to \( R = 5.5 \alpha_0 \), the \( A-X \) band gradually borrows more and more intensity from the \( C-X \) transition, and this explains why the \( \mu_{A-X} \) transition moment slowly but continuously increases in this distance range (see Fig. 3).

The \( \mu_{A-X} \) value computed for the equilibrium distance of the ground state at the lowest possible threshold of \( T = 0.005 \mu E_h \) is 0.021 D. Experimental values for the \( A \rightarrow X \) transition moment, obtained from the measured ratio of the \( B \rightarrow X \) and \( A \rightarrow X \) emission intensities, are 0.014 D at \( R = 2.15 \) \( \AA \) (Ref. 24) and 0.016 D at \( R = 2.18–2.5 \) \( \AA \).\(^{25} \) Taking into consideration that the \( A \rightarrow X \) transition is very weak, the
difference between the theoretical and the experimental results for the $R = 2.15 - 2.18 \text{ Å}$ of about 25% seems to be quite acceptable.

4. $1_u(^3 \Pi - X) - X^1 \Sigma_g^+$

Analogous to the $A \, ^3 \Pi_u - X$ case, the $1_u(^3 \Pi - X$ transition mainly borrows its intensity from the $1 \, ^1 \Pi_u$ admixture to the excited state. Therefore dipole moments for these two transitions have qualitatively similar behavior (see Fig. 3), but the $1_u(^3 \Pi) - X$ transition moment is somewhat weaker. Photoexcitation to the higher-lying $1_u(^4 \Pi, ^5 \Pi$ states is practically negligible due to the fact that the weights of their $A - S$ contributions that could ensure spin-allowed transitions from the $X$ state are extremely small in the Franck–Condon region of the ground state.

C. Absorption spectrum and Cl$^+$/Cl branching ratio

The total extinction coefficient $\epsilon_{\text{tot}}$ computed for the first absorption band of Cl$_2$ ($X, v = 0$) is shown in Fig. 5 along with the experimental data from several studies. In this figure, we also present the $\epsilon_{\text{tot}}$ value calculated for absorption from $X, v = 0, 1$ under assumption of a Boltzmann distribution over the $v = 0, 1$ vibrational levels (the $v = 0$ population is about 7% of that for the $v = 0$ level at room temperature). The position of the maximum and half-width of the computed spectrum from $X, v = 0$ agree with the experimental data of Ref. 9 within several nanometers. The $X, v = 0, 1$ spectrum is slightly broader and its half-width agrees better with the data of Gibson et al. and Seery et al. measured at room temperature. Partial absorption spectra of the weak $B - X$ and $A - X$ transitions are also given in Fig. 5 (see the upper panel). The maximum of the computed $B - X$ band lies at 397 nm ($-25,200 \text{ cm}^{-1}$). This value agrees quite well with the data of Coxon, derived from the absorption spectrum simulation based on the Morse-type extrapolation of the $B$ state Rydberg–Klein–Rees potential to small $R$ values. The discrepancies with the spectrum simulation of Mulliken (23,550 cm$^{-1}$) and Samartzis et al. (24,100 cm$^{-1}$) as well as the theoretical calculations of Yabushita (23,900 cm$^{-1}$) are found to be somewhat larger. Results derived from the measured absorption spectra are subject to considerable uncertainty in this case since the $B - X$ band is overlapped by the much stronger $C - X$ band, but the reason for the disagreement with the theoretical data is unclear. Unfortunately, one cannot directly check the validity of these results, but indirect examination of the computed $B - X$ band can be accomplished by considering the corresponding Cl$^+$/Cl branching ratio calculations, as will be done below.

The branching ratio of the excited and ground state atoms produced in the Cl$_2$ photoabsorption has been calculated in the present work in the adiabatic approximation as

$$\text{Cl}^+/\text{Cl} = \frac{\epsilon(B)}{\epsilon(B) + 2(\epsilon(A) + \epsilon(C))},$$

where $\epsilon(A), \epsilon(B), \epsilon(C)$ are absorption cross sections of the $A, B, C - X$ transitions, respectively. The computed branching ratio function and the corresponding experimental data of $\mu_{B - X}$ and $\mu_{A - X}$ transition dipole moments are slightly overestimated, with this effect being a bit more pronounced for the $B - X$ transition. It is quite difficult to make unambiguous conclusions about the reason for this discrepancy, however, since it is fairly small and too many parameters can influence the final result. This issue is illustrated (see Fig. 6) by comparison of the computed Cl$^+$/Cl branching ratio function with the original fitting of the experimental points made in Ref. 2. The computed branching ratio curve agrees very well with the experimental fitting curve in the $\lambda = 350 - 375$ nm interval, lies slightly lower than the latter at $\lambda < 380 - 405$ nm, almost perfectly matches it at 410–445 nm, and is slightly higher at $\lambda > 450$ nm. One can see that this comparison leads to somewhat different conclusions concerning agreement between theory and experiment with respect to those made above, and thus underlines a point that the calculated results lie practically within the accuracy range of the measured data. Altogether, it can be concluded that the good agreement obtained for the Cl$^+$/Cl ratio with the experimental data in the 350–465 nm range demonstrates that the positions and relative intensities of the $B - X$ and $A - X$ absorption bands are obtained quite accurately in the present study.

IV. CONCLUSION

Ab initio calculations of the potential energy curves and dipole moments for transitions from the $X^1 \Sigma_g^+$ ground state

FIG. 6. Cl$^+$/Cl branching ratio as a function of excitation wavelength: points: experimental results from Ref. 2; dashed line: fitting of the experimental data made in Ref. 2; solid line: computed in this work.
to the lowest $0_u^+$ and five $1_u$ valence excited states have been carried out employing the multireference spin-orbit CI method in combination with RECPs. The computed dipole moment of the perpendicular $C^1\Pi_{1_u} \rightarrow X^1\Sigma_g^+$ transition is found to be very sensitive to the dimension of the CI expansion (or MRD-CI configuration selection threshold), with large CI spaces producing a notable increase in the $\mu_{C-X}$ values. Similar findings have been discussed in Ref. 33 for the $A^2\Pi_{1_u} \rightarrow X^2\Sigma_g^+$ transition moment in HI. In contrast to $\mu_{C-X}$, the dipole moment of the parallel $B^3\Pi_{0_u} \rightarrow X^1\Sigma_g^+$ transition shows only minor changes with MRD-CI selection threshold variation. This is once again similar to the results obtained for the HI molecule (the $a^3\Pi_0^- \rightarrow X^1\Sigma_g^+$ transition), so that it can be concluded that there are strong similarities in the influence of the CI expansion on the accuracy of computed dipole moments for the first absorption band of the hydrogen halide and halogen molecules.

It has been found that the dipole moments of the spin-forbidden transitions vary strongly with $R$. This is especially important for the $\mu_{B-X}(R)$ value, which almost doubles in the Franck-Condon region. This fact has a significant influence on the position of the $B-X$ band maximum as well as on the shape of this band, in particular in its short wavelength part, at $\lambda=300$–350 nm. The computed dipole moments of the $C^1\Pi_{1_u} \rightarrow X^1\Sigma_g^+$ and $B^3\Pi_{0_u} \rightarrow X^1\Sigma_g^+$ transitions show very good agreement with available experimental data obtained at the equilibrium internuclear distance of the ground state ($R=2.0$ Å) and at $R=2.1$ Å, respectively. The $\mu_{B-X}$ value is probably slightly overestimated (by $\leq7\%$) at larger internuclear distances, $R>2.2$ Å. Agreement between the present calculations and experiment for the weakest $A^3\Pi_{1_u} \rightarrow X^1\Sigma_g^+$ transition is somewhat worse, with both the calculated and measured data for this transition being less reliable than for the stronger ones.

The total absorption spectrum of the first Cl$_2$ band and the Cl*$/$Cl branching ratio calculated in the adiabatic approximation as a function of the excitation wavelength agree very well with the experimental data. The computed position of the first absorption band maximum, which is mainly determined by the $C-X$ transition, reproduces the experimental results with an accuracy of 2 nm. The maximum of the $B-X$ absorption band is in good agreement with the value obtained by Coxon, but differs by up to 20 nm from the results obtained in other studies. Good agreement of the calculated Cl$^*$/$Cl$ branching ratio with the experimental data may be taken as an argument in favor of the data obtained in the present work.

Finally, one should mention that the variation of the $B-X$ dipole moment in the Franck-Condon region should have an important influence on the anisotropy parameter $\beta$ for the Cl$^*$ + Cl dissociation channel, which depends on the $B\rightarrow X$ and $C\rightarrow X$ absorption coefficients and on the efficiency of nonadiabatic processes. Unfortunately, our potential energy curves and wave functions at intermediate internuclear distances are not smooth enough for an accurate calculation of the nonadiabatic coupling matrix elements. A rough estimate made in the present study employing data on the Cl$1_u\rightarrow 1_u$(III,IV) nonadiabatic transition probability obtained in the framework of the Rosen-Zener-Demkov model in Ref. 6 shows that the change of the $B\rightarrow X$ absorption spectrum leads to an increase in the $\beta$ values by 0.25–0.50 at $\lambda=320$–350 nm relative to the previous theoretical results. This change brings them in overall better agreement with the experimental data for the $\beta$ parameter in the above excitation range.

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28. P. A. Christiansen, www.clarkson.edu/~acs15/pac/web/cl_large_core.f