An ab initio study of the C H 3 I photodissociation. II. Transition moments and vibrational state control of the I * quantum yields

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An *ab initio* study of the CH$_3$I photodissociation. II. Transition moments and vibrational state control of the I$^\ast$ quantum yields

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Multireference spin-orbit configuration interaction calculations of transition moments from the $\tilde{X}A_1$ ground state to the $3Q_0^+, 1Q_1$, and $1Q$ excited states responsible for the $A$ absorption band of CH$_3$I are reported and employed for an analysis of the photofragmentation in this system. Contrary to what is usually assumed, the $3Q_0^+(A_1)$, $3Q_1(E)$, and $1Q(E)\rightarrow\tilde{X}A_1$ transition moments are found to be strongly dependent on the C–I fragmentation coordinate. The sign of this dependence is opposite for the parallel and perpendicular transitions, which opens an opportunity for vibrational state control of the photodissociation product yields. The computed absorption intensity distribution and the I$^\ast$ quantum yield as a function of excitation energy are analyzed in comparison with existing experimental data, and good agreement between theory and experiment is found. It is predicted that significantly higher I$^\ast$ quantum yield values ($>0.9$) may be achieved when vibrationally hot CH$_3$I molecules are excited in the appropriate spectral range. It is shown that vibrational state control of the I$^\ast$/I branching ratio in the alkyl (hydrogen) iodide photodissociation has an electronic rather than a dynamic nature: Due to a different electron density distribution at various molecular geometries, one achieves a more efficient excitation of a particular fragmentation channel rather than influences the dynamics of the decay process. © 2007 American Institute of Physics

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I. INTRODUCTION

The I$^\ast$ atom quantum yield $\Phi_I^\ast(\lambda)$ as defined in Eq. (2) of the preceding article (called Paper I hereafter) is the most important quantity describing the alkyl iodide dissociation process in their $A$ absorption band. Therefore, it is not surprising that its experimental determination attracted great attention from researchers in the last three decades.$^{1-23}$ A large variety of experimental techniques have been applied to measure $\Phi_I^\ast(\lambda)$ values including time-of-flight mass spectrometry,$^{1,12,15}$ (TOFMS), state-selective ionization and pulsed-field TOFMS,$^{21}$ vacuum absorption,$^{1,2}$ laser-induced fluorescence,$^{11,19,20}$ IR emission,$^{7-9}$ photoacoustic spectroscopy,$^{5,6}$ gain versus absorption spectroscopy,$^{16}$ and resonant-enhanced multiphoton ionization.$^{22-24}$ These studies have shown that the problem of accurate experimental determination of the $I^\ast$ quantum yield (or I/I$^\ast$ branching ratio of the final products) and its dependence on excitation energy is not a trivial task, especially when a final product should be unambiguously associated with a particular dissociation channel on the basis of measured data.

The first I$^\ast$ quantum yield determination has been carried out by Riley and Wilson$^{1}$ employing time-of-flight spectroscopy at a single wavelength (266 nm). They have obtained $\Phi_I^\ast(266\text{ nm})=0.79\pm0.11$, although the accuracy of the measurements was fairly modest at that time. This work has been followed by a number of studies in which both broadband excitation$^{2,3}$ or excitation at some particular light wavelengths have been used.$^{4,5,7-9,11-16}$ The most numerous measurements of $\Phi_I^\ast(\lambda)$ have been done in the center of the $A$ band at $\lambda=266$ and 248 nm, which is explained by the availability of suitable lasers at these energies. The maximum of the total $A$ band absorption spectrum is located at $\sim258$ nm,$^{7,25-28}$ so that the above two wavelengths characterize the I$^\ast$ quantum yields at slightly lower and higher energies. In both cases the $\Phi_I^\ast$ values are measured to lie between 0.70 and 0.81, with the overall spread of the measured data being around 10%.

Very little is known about the I$^\ast$/I branching ratio at $\lambda<248$ nm (only two points, $\lambda=240$ and 222 nm, are available), whereas at $\lambda\gg266$ nm this information is much more abundant. It shows that $\Phi_I^\ast$ decreases rather quickly at long wavelengths, becoming $<0.05$ for $\lambda>305$ nm. The discrepancy in the measured $\Phi_I^\ast$ values is notably higher in this excitation energy range, however. One can also note that there are only two studies in which the I$^\ast$ quantum yields have been determined at more than two wavelengths, Refs. 5 and 22, and even in these cases the number of $\lambda$ points studied has been pretty limited (five and four wavelengths, respectively).

From the analysis of the available experimental data, one may conclude that although great effort has been invested in determination of the I$^\ast$ quantum yields the obtained $\Phi_I^\ast$ data are still incomplete and in some cases are characterized by fairly large discrepancies and possibly systematic errors. The reasons for such errors may be (i) wrong calibration of the absolute $\Phi_I^\ast$ values, (ii) contributions of vibrationally hot...
parent molecules, and (iii) possible CH₃I cluster formation, which can substantially influence the accuracy of the obtained data.

The main goal of the present study is to obtain ab initio information for the A absorption band of CH₃I at a level of accuracy which allows one to analyze the entire photodissociation process from first principles. In the first part of this work (Paper I) we have reported potential energy surfaces (PESs) calculated for the low-lying valence and Rydberg states. In the second part (this article) the calculated data for transition moments responsible to the A-band absorption are presented and combined with the PES data from Paper I to obtain partial and total absorption spectra and the I⁰ quantum yields.

II. DETAILS OF THE THEORETICAL TREATMENT

The computational method employed in the present study is based on a combination of the multireference configuration interaction (CI) approach and relativistic effective core potentials (RECPs) and has been described in general in the first part of this work. Details concerning atomic basis sets, RECPs employed, relevant geometries and self-consistent field calculations have also been given in Paper I.

There are two techniques suitable for including spin-orbit (SO) coupling in the present computations. The first approach involves forming a matrix representation of the full relativistic Hamiltonian in the basis of the A-S wave functions. It can be viewed as a CI method employing a heavily contracted many-electron basis. It works especially well in applications such as the present one in which the SO interaction is essential but still of secondary importance compared to terms in the nonrelativistic Hamiltonian [A-S contracted SO-CI or simply LSC-SO-CI (Ref. 29)]. It should be noted that in this procedure the diagonal Hamiltonian matrix elements do not have SO contributions and are simply the energy eigenvalues of the various A-S wave functions. For this purpose the estimated full CI results are used, that is, to which the Davidson correction has been applied. The off-diagonal SO matrix elements are computed with the variational eigenfunctions. The above procedure also has the advantage of allowing a direct analysis of the final spin-perturbed electronic wave functions in terms of their A-S components. Transition moments between the final double group symmetry states are obtained by the transformation of the corresponding A-S results mentioned above.

The above computational approach has been employed in Paper I to obtain PESs of the low-lying valence and Rydberg states relevant to the problem discussed. Our earlier study of the analogous HI system has shown, however, that an accurate calculation of the related transition moments, particularly for the parallel state transition, requires inclusion of a large number of higher-lying A-S states which are mixed by the SO interaction with the A-band states. Therefore, the LS-SO-CI calculations have been carried out in the present study for a much larger number of roots (17–18 roots per symmetry) for all four singlet and triplet Cs irreducible representations. Unfortunately, the corresponding selected CI spaces increase drastically in this case, which makes such computations extremely time consuming. Therefore, these calculations have been performed with a larger selection threshold of T=1.25 μEh. Technical details of the above computations are given in Table I.

Although a fairly large number of A-S roots have been included in this procedure and the CI spaces treated explicitly are quite large, it is hard to be certain in this approach if all higher-lying states which can give non-negligible contributions to the transition moments are taken into account. As will be shown below, the transition moment as a function of the C–I distance calculated with the above approach is not very smooth, which can be an indication that some minor but nevertheless important contributions are missing. This problem will be discussed in more detail in the next section.

Therefore, to provide additional independent data for the transition moments, a more demanding multireference spin-orbit configuration interaction (MR-SO-CI) method has also been employed in the present study. In this approach, Coulomb, exchange, and SO interactions are treated simultaneously on an equal footing, and a much larger secular equation is solved, in which all selected configurations of various space and spin symmetries form the basis for the MR-SO-CI calculations, without first obtaining correlated A-S functions. In this particular case, the MR-SO-CI calculations have been carried out in the A’ IR of the Cs double group at a selection threshold of T=1.25 μH. The selection procedure has been performed with respect to a fairly large number of roots (15 per A-S symmetry), which is important to obtain accurate values for the transition moments. The corresponding reference spaces include 85, 88, and 95 configurations for the 1A’, 3A’, and 1A” spaces, respectively, and the generated number of symmetry-adapted functions (SAFs) vary from 23×10⁶ to 58×10⁶ depending on the A-S symmetry. The selected CI spaces lie in between 3×10⁵ and 5×10⁵ SAFs depending on symmetry and C–I distance, while the size of the full secular matrix diagonalized in these computations varies from 1.2×10⁹ SAFs at R=5.5d₀ to 1.8×10⁶ SAFs at R=7.35d₀. More details of both SO-CI methods employed may be found elsewhere.

The final stage of the present computational scheme involves fitting the resulting potential energy curves to polynomials which serve as potentials in the nuclear motion Schrödinger equations to be solved numerically. The vibrational wave functions obtained for the bound ground state and repulsive states of the A band are combined with the corresponding transition moments to compute extinction co-

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FIG. 1. Calculated dipole moments for the \( \tilde{X} \) \( 1A_1 \), \( \tilde{X} \) \( 3Q \), and \( \tilde{X} \) \( 1Q \) states of CH\(_3\)I. Data calculated without spin-orbit coupling: \( \bullet \), \( \tilde{X} \) \( 1A_1 \); \( \bigcirc \), \( \tilde{X} \) \( 3Q \); +, \( \tilde{X} \) \( 1Q \); including spin-orbit coupling: \( \times \), \( \tilde{X} \) \( A_1 \).

The calculated dipole moments \( \mu \) are presented for the \( \tilde{X} \) \( 1A_1 \) ground state (at the \( \Lambda \)-S and \( \Omega \) level) and for the \( \tilde{X} \) \( 3Q \) and \( \tilde{X} \) \( 1Q \) states (only \( \Lambda \)-S results) as functions of the C–I distance in Fig. 1. These data have been obtained at the ground state relaxed geometry with respect to the umbrella angle \( \alpha \); i.e., \( \alpha \) has been optimized for every C–I separation. The calculated data show that the ground state is characterized by a fairly large positive \( \mu \) value, corresponding to a negative charge on the I atom, which increases when CH\(_3\) and I are taken apart. It reaches its maximum at \( R_{C-I} = 5.4a_0 \) before vanishing at the dissociation limit. The final \( \mu \) value at the \( \Omega \) level of treatment for the ground state equilibrium geometry is 0.6958\( e \)\( a_0 \) (1.768 D), which agrees fairly well with the experimental result of 1.6434 D.\(^{35}\) It can also be seen in Fig. 1 that inclusion of SO coupling leads to smaller dipole moment values for the ground state in the entire range of inter-nuclear distances, with this effect being more pronounced at larger C–I separations. This is mainly caused by the SO mixing of the \( \tilde{X} \) \( 1A_1 \) and \( \tilde{X} \) \( 3Q \) states, which becomes stronger at large bond lengths (see Table III in Paper I).

The \( \tilde{X} \) \( 3Q \) and \( \tilde{X} \) \( 1Q \) excited states are characterized by very small positive dipole moment values in the middle of the Franck-Condon (FC) region, which quickly become negative at \( R_{C-I} > 4.2a_0 \). The reason for this is that electron excitation from the lone-pair \( n(e) \) orbital localized on the iodine atom to the antibonding \( \pi^* \) orbital, which is very much shifted toward the CH\(_3\) radical, leads to a significant redistribution of the electron density in the molecule. It causes a sign change of the \( \tilde{X} \) \( 1Q \) dipole moments relative to that of the ground state, indicating a negative charge density on the CH\(_3\) radical. This, in turn, means that the difference of the \( \tilde{X} \) \( 3Q \) and \( \tilde{X} \) \( 1A_1 \) dipole moments is quite large (0.671\( e \)\( a_0 \) at \( R_{C-I} = 4.04a_0 \) and becomes notably larger at longer \( R_{C-I} \), e.g., \( \Delta \mu = 1.265e \)\( a_0 \) at \( R = 4.75a_0 \), which results in a fairly large contribution to the \( \tilde{X} \) \( 3Q \) transition moment. Changes in the dipole moments at short C–I distances are caused by the interaction of the A-band states with the low-lying Rydberg states. It is worth noting that all dipole moment data presented in Fig. 1 have been calculated in the framework of the LSC-SO-CI approach. Test calculations carried out employing the MR-SO-CI treatment have shown that changes in the dipole moment results are fairly small and not decisive for the description of the A-band absorption.

The calculated transition moments for the parallel and perpendicular transitions of the A band as functions of the C–I distance for the optimized ground state geometry are shown in Figs. 2 and 3, respectively. It is well known that transition moments are much more sensitive to the quality of CI and SO treatments than are potential energies. Therefore, the corresponding transition moments for the A-band states have been obtained in the present study employing two computational approaches, LSC-SO-CI and MR-SO-CI, and convergence of the calculated data with respect to the variation of the computational parameters has been analyzed.

The \( \tilde{X} \) \( 3Q \) and \( \tilde{X} \) \( 1Q \) \( Q_0 \) transition polarized parallel to the CH\(_3\)I molecular axis plays the key role in the A band since it is directly responsible for the CH\(_3\)+I\((a^2P_{1/2})\) dissociation channel. The calculations carried out with both methods find that the \( \tilde{X} \) \( 3Q \) transition moment increases rather quickly with \( R_{C-I} \) in the FC region (Fig. 2). At \( R_{C-I} < 2.18 \) Å the MR-SO-CI method gives somewhat larger \( \mu(Q_{0 \rightarrow \tilde{X}}) \) values, while at longer C–I distances the situation is opposite. It can...
be seen in Fig. 2 that the LSC-SO-CI approach provides a somewhat unsmooth functional dependence on the C–I distance. Unfortunately, it was not possible to carry out a complete set of the present LSC-SO-CI calculations at a threshold lower than $T=1.25 \mu E_b$. Therefore, in order to check the convergence of the $A$-band transition moments with respect to the size of CI and SO treatments, additional test calculations have been performed for selection thresholds as low as 0.5 $\mu E_b$ and number of roots up to 22 per $A$-$S$ symmetry. These calculations have not shown any definite trend for the $\mu(3Q_{0+}^r-\tilde{X})$ values, indicating, however, fairly high sensitivity (up to 10% variation) with respect to the number of roots treated. This means that SO mixing with high-lying states is important to obtain accurate $\mu$ values, and ordering of the roots changing with C–I distance is responsible for the unsmooth $\mu(R_{C-I})$ functional dependence. Therefore, it has been decided to use the $\mu(3Q_{0+}^r-\tilde{X})$ values obtained at $T=1.25 \mu E_b$ applying a polynomial fitting procedure, while the above results give an estimate for the accuracy of its determination.

The above problem does not exist in the MR-SO-CI calculations where correlation and SO are treated on an equal footing, which allows one to include configuration states having strong SO coupling with states of interest in a consistent manner and leads to a much smoother $\mu(R_{C-I})$ dependence. The size of the corresponding secular matrix can become very large in this case, however, so that one has to sacrifice the accuracy of the correlation treatment in this approach in order to make the treatment feasible. This can be seen, for example, from the fact that when a number of roots for which the selection procedure is employed is increased, this leads to fairly strong changes in the $\mu$ values. The final results in the MR-SO-CI calculations have been obtained at $T=1.25 \mu E_b$ and 15-root selection.

Altogether, one can conclude that it is hard to favor one or the other method (LSC-SO-CI versus MR-SO-CI) for transition moment calculations since both of them have their advantages. Therefore, it has been decided to use the average $\mu(3Q_{0+}^r-\tilde{X})$ values obtained with the two methods to calculate the partial absorption spectrum for the $3Q_{0+}$ state. The $\mu(3Q_{0+}^r-\tilde{X})$ values obtained in both types of calculations (computed points) are given in Table II together with the fitted and averaged data. The same averaging procedure has also been used for the calculation of the perpendicular transitions to the $1Q$ and $3Q_1$ states, although discrepancies between the two methods employed are smaller in this case.

As already mentioned, the composition of the parallel $3Q_{0+}^r-\tilde{X}A_1$ transition is quite complicated in the FC region. It is a sum of at least four fairly strong $A$-$S$ contributions which vary significantly with $R_{C-I}$ distance, while a number of other, minor contributions are non-negligible as well. Near the $\tilde{X}A_1$ equilibrium $R_{C-I}$ value (4.04$\sigma_0$), it is found that the largest contributions to this quantity come from dipole moments of the key $\tilde{X}A_1$ and $3Q$ states, as well as from various transition moments connecting each of these $A$-$S$ states to higher-lying valence and Rydberg states of the same respective symmetry (roots number 7, 10, and 13 in the $1A'$ representation). For this reason it was important to include a fairly large number of such excited states in the final LSC-SO-CI

![FIG. 2](image-url) Calculated electric-dipole moment for the $3Q_{0+}^r-\tilde{X}A_1$ transition in CH$_2$I: ×, LSC-SO-CI (dashed line, fitting); •, MR-SO-CI (dotted line, fitting); solid line, the averaged $3Q_{0+}^r-\tilde{X}A_1$ value (see text). The dotted vertical line corresponds to the ground state equilibrium geometry.

![FIG. 3](image-url) Calculated electric-dipole moments for the $1Q$, $3Q-\tilde{X}A_1$ transitions in CH$_2$I: ○, $1Q-\tilde{X}$ (solid line, fitting); ×, $3Q-\tilde{X}$ (dashed line, fitting). The dotted vertical line corresponds to the ground state equilibrium geometry.

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treatment. For example, at the equilibrium $R_{C-I}$ value, the direct mixing of the $3Q$ and $X^1A_1$ states and the $3Q-\bar{3}A_1$ (valence) mixing are responsible for 30% of the total transition moment each, while various Rydberg states give the remaining 40%. At a much larger $R_{C-I}$ value of 4.75$\alpha_0$, it is found that the first two contributions clearly dominate (42% and 46%, respectively), whereas at short C–I distances contributions of the Rydberg states become more important.

The calculated averaged values for the perpendicular transitions are shown in Fig. 3. The main A-S contribution to the $3Q_1-1Q-X$ transition moments comes from the $1Q-\bar{3}A_1$ transition, which, in turn, is mainly determined by the one-electron $n(e)-\alpha_i^e$ electric dipole matrix element. The $n$ molecular orbital (MO) has a primarily iodine atomic $p$ character until relatively short $R_{C-I}$ distances. Even though the $\alpha_i^e$ is notably more delocalized, the result is that the above matrix element is relatively small for $R_{C-I}\approx 4.5\alpha_0$ because it corresponds mainly to an atomic transition between different components of the iodine $5p$ orbital. This situation begins to change around $R_{C-I}\approx 4.5\alpha_0$ because both the $e$ and, in particular, $\alpha_i^e$ MOs become significantly more delocalized as the two atoms approach each other. This means that the $1Q-X$ transition moment is changing rapidly in the FC region of $\tilde{X}A_1$, thus making it an especially important factor in computing the desired intensity distribution in the A band of CH$_3$I, as it was also the case for HI. Because the $3Q_1-\tilde{X}$ transition derives the major part of its intensity by borrowing it from $1Q-\tilde{X}$, its transition moment also starts to increase fairly rapidly in the same region of C–I distance, although its magnitude is generally only about half as large (see Fig. 3).

There is one more state, $3A_1(E)$, transition to which may be important for describing the A absorption band. The excitation energy analysis carried out in Paper I shows, however, that this state lies too high to make any significant contribution to the A band. It is possible that absorption to this state is partly responsible for the high-energy tail of the band at $E>46\,000$ cm$^{-1}$, but absorption at such energies is very weak, <5% of the band maximum, and this effect will not be analyzed in the present study.

Finally, it is worthwhile to note that it has been a common practice in earlier attempts to analyze the composition of the absorption spectrum and the $1/1^*$ branching ratio of this system to simply assume constant values for these quantities over the entire range of bond distance (see, e.g., Ref. 36). It is apparent from the present $ab\ iniito$ results that this is a poor approximation, especially in the FC region of the $\tilde{X}A_1$ state.

IV. ABSORPTION SPECTRA AND QUANTUM YIELDS

A. Partial and total absorption spectra

When potential energy surfaces calculated in Paper I are combined with the present transition moment results, partial extinction coefficients for transitions from $\tilde{X}A_1, v''=0$ to the A-band states can be obtained as functions of excitation energy. They are shown in Fig. 4, while the corresponding absorption parameters are summarized in Table III. Since an electronic excitation process is very fast in comparison with the motion of the nuclei, the spectral calculations have been carried out at the ground state optimized geometry.

The onset for the A-band absorption occurs at about 32 000 cm$^{-1}$ (312 nm), at which energy the total extinction coefficient is around 1.0% of its maximal value. As can be seen in Fig. 4, only the $3Q_1$ state can be excited at such energies. The corresponding starting point for the $3Q_{0^*}-\tilde{X}$ transition lies about 2000 cm$^{-1}$ higher, while the $1Q-\tilde{X}$ onset occurs at 36 500 cm$^{-1}$. The $3Q_1$ state has a very broad and flat absorption curve, with a maximum at $\approx 35\,800$ cm$^{-1}$. The $3Q_{0^*}-\tilde{X}$ absorption reaches its maximum at $\approx 38\,900$ cm$^{-1}$, at which point it clearly dominates the A band [$e_{\text{max}}(3Q_{0^*})=238.7$ l mol$^{-1}$ cm$^{-1}$]. The maximum in the $1Q-\tilde{X}$ absorption is computed to occur near 42 200 cm$^{-1}$, which is notably higher than the vertical excitation energy from the $\tilde{X}, v''=0$ level (41 450 cm$^{-1}$). This can be easily explained by the fast increase in the $1Q-\tilde{X}$ transition moment in the FC region (Fig. 3).

The total absorption curve calculated as a sum of transitions to the $3Q_1, 3Q_{0^*}$, and $1Q$ states is shown in Fig. 4 as well, where it is compared with the experimental data. The maximum of the A-band absorption spectrum is measured to be $e_{\text{max}}=285-320$ l mol$^{-1}$ cm$^{-1}$ (Refs. 7 and 25–28) and lies

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$^a$Calculated with energy adjustments (see text).

FIG. 4. Calculated partial absorption spectra for transitions from $\tilde{X}A_1, v''=0$ to the $3Q_1$, $3Q_{0^*}$, and $1Q$ states and the total absorption spectrum of the A band: Dash-dotted line, calculated; solid line, calculated including adjustments (see text); points, experimental data (see the inset in the figure).

TABLE III. Calculated characteristics for the partial and total absorption spectra of the A band in comparison with the experimental data.
at \(\approx 258\) nm (38 760 cm\(^{-1}\)). One can note a fairly large discrepancy in the experimental \(\varepsilon_{\text{max}}\) values, while the position of the \(A\)-band maximum determined in the above studies agrees within 100 cm\(^{-1}\). The corresponding computed values of 276 l mol\(^{-1}\) cm\(^{-1}\) and 39 020 cm\(^{-1}\) are in very good agreement with experiment. The overall shape of the theoretical absorption curve (the long-dashed curve in Fig. 4) is very similar to the observed one, except for a slight shoulder in its blue part at energies beyond 42 000 cm\(^{-1}\).

From the above discussion it is quite clear that the total absorption curve depends on a large number of fine details such as shapes and locations of potential curves for the various electronic states, as well as the variation of the respective transition moments. It is not very difficult to achieve an almost perfect agreement of the experimental and calculated total absorption curves with so many adjustable parameters available. Positions and maxima of the above three states alone give six such parameters. In view of the present situation it has been decided, however, not to make any major adjustments of the calculated data. There are two small corrections which seem to be well grounded from the theoretical point of view. One of them concerns the relative position of the \(1^Q\) state because of the difficulty of calculating correlation energies of singlet states at the same level of accuracy as triplets. In the present case we estimate that there is a bias of about 800–1000 cm\(^{-1}\) due to the overestimation of the \(1^Q\) excitation energy with respect to the \(3^Q\) states. This estimate is based on the underestimation of the \(\tilde{X}A_1\) ground state correlation energy (see Paper I), as well as on the analogy with the HI molecule, where the same effect has been observed.\(^{32}\) There is one more source for a small systematic error in the present calculations. It results from the influence of the spectator vibrations, e.g., umbrella and bending vibrations, on the position of the absorption spectrum, which have not been explicitly included in the calculations. The fundamental frequencies of the \(v_3(a_1)\) umbrella vibration for the excited \(1^{13}Q\) states calculated in the first part of this work (Paper I) is found to be 50–100 cm\(^{-1}\) lower than the \(v_3\) value for the \(\tilde{X}A_1\) ground state. The frequency of the \(v_3(e)\) bending mode has not been determined in the present study, but we suppose that it is also smaller than that of the ground state by approximately the same margin. Altogether, this must result in a shift of the total absorption spectrum by \(\approx 200\) cm\(^{-1}\). Therefore, we have carried out the intensity calculations in a second treatment which differs from that already discussed by a downward shift of the \(1^Q\) potential energy curve by 900 cm\(^{-1}\) and of the total spectrum by 200 cm\(^{-1}\).

The results of the calculation with these two adjustments are shown as a solid line in Fig. 4. One can see that the shoulder at the high-energy slope of the absorption curve disappears and there is also some improvement in the agreement of the computed data (\(\varepsilon_{\text{max}}=294.4\) l mol\(^{-1}\) cm\(^{-1}\), \(v_{\text{max}}=38830\) cm\(^{-1}\)) with the measured absorption in the middle of the band. The second adjustment actually has a fairly small impact on the spectrum, just slightly improving the position of the total absorption maximum. A more critical test of the accuracy of the calculations is provided by the experimental data for the product distribution in the \(\text{CH}_3\text{I}\) photodissociation, as will be discussed in the next section.

**B. Quantum yields and polarization**

The calculated results for the quantum yield of excited iodine atoms \(\Phi_{1}(\nu)\) are compared with available experimental data in Fig. 5. The theoretical values are obtained by taking the ratio of the extinction coefficients for the \(3Q_{0^\nu}\) \(\leftarrow \tilde{X}, \nu''=0\) transition to the total

\[
\Phi_{1}(\nu) = \frac{\varepsilon(3Q_{0^\nu})}{\varepsilon(3Q_{0^\nu}) + \varepsilon(1Q_1) + \varepsilon(1Q)}.
\]

We have included experimental data from 12 different groups\(^{14–24}\) in Fig. 5, which have been reported over a period of 30 years. The calculated \(\Phi_{1}\) values have been obtained employing the two theoretical adjustments described above. One can see that the calculated data agree fairly well with the experimental results in the middle of the band, \(\lambda=248–275\) nm. The maximal \(\Phi_{1}\) value is calculated to be 0.83 and it lies at 266 nm. This is slightly higher than 0.71–0.78 measured at this wavelength. There is also a good agreement between the various experimental results (0.59–0.81) and the theoretical value (0.62) on the high-energy side, at 248 nm. Discrepancies between the calculated and measured data become somewhat larger on the low-energy side of the \(\Phi_{1}(\nu)\) curve, for \(\nu=(32–34)\times 10^3\) cm\(^{-1}\). This may be caused, for example, by some overestimation of the intensity of the weak \(3Q_{1}\) partial spectrum or an error in its calculated position. It is worth noting, however, that the total absorption is very weak in this energy range, e.g., only \(\approx 1.5\%\) of \(\varepsilon_{\text{max}}\) at 300 nm. This makes accurate \(\Phi_{1}(\nu)\) measurements very difficult, which is also indicated by the strong spread of the experimental data for \(\lambda=296–312\) nm. There could be more physically meaningful reasons for the above discrepancy, which will be discussed in more detail below.

The present calculations have been carried out in the adiabatic approximation, and therefore the angular distribu-
tion of the photodissociation products is determined solely by the optical excitation. The prediction of the calculations with regard to $\beta$ anisotropy coefficients is quite clear in this case. The $^1I$ atom product results exclusively from the parallel transition $^3Q_0^\alpha(A_1) \rightarrow \tilde{X}A_1$. This is in good agreement with previous experimental studies, which find $\beta$ values near 2 throughout the $A$ band. The situation for the I atom product must be equally clear, namely, that it results from the perpendicular $^3Q_1, ^1Q(E) \rightarrow \tilde{X}A_1$ transitions, and thus the angular distribution in the I dissociation channel must be characterized by the $\beta=-1$ value. Experimental results are not so unambiguous in this case, however. In many studies positive $\beta$ values have been measured for this channel (see, e.g., Ref. 22), which also have been found to be dependent on the excitation energy. Therefore, this matter deserves a brief discussion.

There are two possibilities to obtain I atoms from the parallel channel. One of them is provided by photoexcitation to the $^3Q_0^\alpha$ state (A$_1$ symmetry in the C$_{3v}$ group) and subsequent nonadiabatic transition to $^1Q(E)$, which is possible due to the crossing (conical intersection) of the above two states (see Fig. 2 in Paper I). This crossing lies very low ($T_0 = 32.950$ cm$^{-1}$) in the $A$ band, however, and the corresponding nonadiabatic coupling has a spin-rotational nature if the CH$_3$I molecule retains its symmetric top geometry in the dissociation process. Such coupling may be strong only in the case of very rotationally hot CH$_3$I molecules. If the $v_b(e)$ bending mode becomes active, this leads to lowering of the overall symmetry to C$_1$ and thus to the $^1Q$ splitting into its $A'$ and $A''$ components. The $^1Q(A')$ state is connected to the $^3Q_0^\alpha(A')$ state by the radial coupling in this case. Therefore, one can suppose that in the case of strong bending vibrations, the nonadiabatic $^3Q_0^\alpha(A') \rightarrow ^1Q(A')$ transitions become much more efficient.

The second possibility for obtaining I atoms from channels with parallel polarization is provided by the $\mu_z$ contributions to the $^3Q_2, ^3Q_1, ^1Q(E) \rightarrow \tilde{X}A_1$ transitions, which become nonzero in the case of molecular symmetry lowering to C$_1$, due, e.g., to the bending vibrations. They can contribute to the $^3Q_2, ^3Q_1, ^1Q(A') \rightarrow \tilde{X}A'$ transitions in this case, which is normally overlooked in the A-band polarization analysis. Test calculations carried out in the present work show, however, that such contributions can become important. For example, it has been found that the parallel $\mu_z$ component of the $^3Q_2(A') \rightarrow \tilde{X}A'$ transition moment computed at the ground state equilibrium $R_{C-I}$ and $\alpha$ values and bending angle $\theta=10^\circ$ becomes notably larger than the $\mu_{zz}$ contributions to the $^3Q_1(A') \rightarrow \tilde{X}A'$ transition (0.0567 $e\alpha_0$ vs 0.0413 $e\alpha_0$) which otherwise dominate the low-energy part of the $A$ band. Altogether, it is clear that a detailed analysis of the product angular distribution requires very time-consuming calculations of multidimensional PESs (at least four dimensional), the corresponding transition and coupling matrix elements. It was not the purpose of the present work to study this effect at a quantitative level.

![Figure 6](image6.png)

**FIG. 6.** Calculated partial absorption spectra for transitions from $\tilde{X}A_1$, $v''=1$ to the $^3Q_1, ^1Q_0^\alpha$, and $^1Q$ states and the total absorption spectrum.

**C. Quantum yields for $\tilde{X}, v'=1, 2$ and vibrational state control of photodissociation products:** $\Phi_T(\lambda)$, temperature dependence

As has been discussed in Sec. III, the calculated dipole moments for perpendicular ($^3Q_1, ^1Q\rightarrow \tilde{X}$) and parallel ($^3Q_0^\alpha\rightarrow \tilde{X}$) transitions show opposite dependence on the C–I distance. This allows one to surmise that excitation from the vibrationally hot ground state of CH$_3$I may lead to significantly higher $^1I$ quantum yields, at least on the low-energy side of the $A$ band, where transitions to the $^3Q_0^\alpha$ state must clearly dominate. The calculated partial and total absorption spectra for excitation from $\tilde{X}, v''=1$ and 2 are shown in Figs. 6 and 7, respectively, and the corresponding $\Phi_T(v')$ values are given in Fig. 8. One can see that the low-energy part of the total spectrum for the $v''=1, 2$ levels indeed is dominated by the parallel $^3Q_0^\alpha\rightarrow \tilde{X}A_1$ excitation, while the blue part of the spectrum is characterized by the competition between the $^3Q_0^\alpha\rightarrow \tilde{X}$ and $^1Q\rightarrow \tilde{X}$ transitions. The obtained data also show that it is possible to achieve the $^1I$ quantum yield val-
ues up to 0.9 ($v''=1,2$) upon excitation in the appropriate spectral range: around $(34–35)\times10^3 \text{ cm}^{-1}$ for $v''=1$ or $(31.5–35.5)\times10^3 \text{ cm}^{-1}$ for $v''=2$. This opens a possibility for vibrational state control of the photodissociation products by an initial population of some particular vibrational level and subsequent UV excitation in the appropriate energy range. The same effect has been predicted earlier in our calculations of the HI molecule$^{32}$ and has later been confirmed experimentally for $v''=2$. In our later note on this system$^{38}$ it has been additionally shown that a slight adjustment of relative positions of the singlet and triplet states of the A band, analogous to that made in the present study, allows one to obtain an almost perfect agreement of the ab initio and experimental $\Phi_T(\nu)$ values.

From the above $1^-$ quantum yield data for the $v''=1,2$ levels it is clear that the $\Phi_T(\nu)$ values must exhibit a significant temperature dependence. The $v_3$ frequency ($534 \text{ cm}^{-1}$) is the lowest among the six vibrational modes of the CH$_3$I molecule and therefore must play the most important role when the temperature is increased. The $v_6$ mode may be of interest in this respect as well, but its frequency is notably higher, $883 \text{ cm}^{-1}$, and for simplicity it will be neglected in the present analysis.

The total A-band absorption spectrum calculated employing the Boltzmann distribution over $v_3$ vibrational levels at various temperatures ($T=0–333 \text{ K}$) is shown in Fig. 9. One can see that the temperature increase leads to absorption decrease in the middle of the band, but, more interestingly, to a strong relative increase of absorption in the red part of the band. The explanation is quite simple. As noted above, the $v_3$ vibrational quantum is relatively small and, as a result, notable fractions of the molecules, e.g., 7.6% and 0.6% at room temperature ($T=298 \text{ K}$), are in the $v''=1$ and 2 vibrational levels, respectively. The fast increase of the $3Q_{0v}\leftarrow\tilde{X}A_1$ transition moment with the C–I distance in the FC region leads to a significant absorption growth in the low-energy part of the band. In contrast, the temperature influence on the blue part of the spectrum is notably smaller since the increase of the $1Q_{0v}\leftarrow\tilde{X}$ transition moment at short $R_{\text{C-I}}$ separations is compensated by a decrease in the $3Q_{0v}\leftarrow\tilde{X}$ transition and the steepness of the $1Q$ PES which leads to redistribution of the absorption intensity over a large energy interval. A comparison with available experimental data$^{26,27}$ shows that the above theoretical findings are in very good agreement with the absorption spectrum measurements.

The $\Phi_T(\nu)$ values calculated for $T=0$, 243, 298, and 333 K under the above assumptions are shown in comparison with experimental data in Fig. 10 and are summarized for a number of wavelengths for which experimental $\Phi_T(\nu)$ values are available in Table IV. It can be seen that the temperature increase significantly improves the agreement with the experimental $1^-$ quantum yields in the low-energy part of the A band, mostly obtained at room temperatures. Further temperature increase up to 333 K leads to even higher $\Phi_T(\nu)$ values for $E\leq36\times10^3 \text{ cm}^{-1}$, while in the middle of the band they become slightly smaller, also improving the agreement with experiment. One can conclude that the strong (and opposite!) dependence of the perpendicular and parallel transi-
TABLE IV. Calculated \( \Phi_T(\lambda) \) quantum yield values for the \( \text{CH}_3\text{I} \) photodissociation in the \( \text{A} \) band in comparison with the experimental data.

<table>
<thead>
<tr>
<th>( \lambda (\text{nm}) )</th>
<th>( T=0 \text{ K} )</th>
<th>( T=298 \text{ K} )</th>
<th>Expt.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>222</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>0.63±0.02</td>
<td>19</td>
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<td>240</td>
<td>0.39</td>
<td>0.40</td>
<td>0.68±0.07</td>
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<td>0.64</td>
<td>0.65</td>
<td>0.59±0.04</td>
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<tr>
<td>248</td>
<td>0.65</td>
<td>0.66</td>
<td>0.81±0.04</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.71±0.04</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>251.5</td>
<td>0.73</td>
<td>0.73</td>
<td>0.60±0.04</td>
<td>5</td>
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<tr>
<td>254</td>
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<td>0.77</td>
<td>0.81±0.10</td>
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<tr>
<td>266</td>
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<td>0.82</td>
<td>0.78±0.11</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.73±0.04</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.71±0.03</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>275.5</td>
<td>0.73</td>
<td>0.75</td>
<td>0.76±0.09</td>
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<tr>
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<td>5</td>
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<tr>
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<tr>
<td>304</td>
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<td>0.15</td>
<td>0.43</td>
<td>17</td>
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<tr>
<td></td>
<td></td>
<td>0.30</td>
<td>Ref. 21</td>
<td></td>
</tr>
<tr>
<td>305</td>
<td>&lt;0.01</td>
<td>0.13</td>
<td>0.20</td>
<td>22</td>
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<tr>
<td>308</td>
<td>&lt;0.01</td>
<td>0.09</td>
<td>0.05</td>
<td>7</td>
</tr>
<tr>
<td>312.5</td>
<td>&lt;0.01</td>
<td>0.05</td>
<td>0.19±0.04</td>
<td>5</td>
</tr>
<tr>
<td>333</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.05</td>
<td>18</td>
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</tbody>
</table>

D. Quantum yields: HI and CH\textsubscript{3}I comparison

From a comparison of the theoretical data obtained in this work and in our earlier study of HI,\textsuperscript{32} it is clear that photodissociation of the HI and CH\textsubscript{3}I molecules in their \( \text{A} \) absorption bands is qualitatively very similar. It is well known, however, that the maximal \( \Gamma^* \) quantum yield values in the middle of the bands differ quite strongly for these two systems, 0.73–0.78 in CH\textsubscript{3}I versus 0.51 in HI. Therefore, it is of great interest to find an explanation for this effect.

An answer can be obtained only from the detailed comparative analysis of both systems. As can be seen in Paper I and our earlier HI study,\textsuperscript{32} excitation energies and relative positions of the \( 3\text{Q}_0^*, \text{Q}_0^*, \) and \( \text{Q} \) states responsible for the \( \text{A} \)-band photodissociation show no significant distinctions. The \( 3\text{Q}_0^* \) PES possesses a shallow minimum in both cases, which lies outside the Franck-Condon region. It has also been shown that excitation to the \( \text{r}^{3}\Sigma^+_1 [E(3\text{^2}A_1)] \) state does not play any role in the \( \text{A} \) band, except maybe in the high-energy tail of the band. The \( 3\text{Q}_0^*, 3\text{Q}_1^*, 4\text{Q}→\tilde{X} \) transition moments are characterized by a strong distance dependence in both systems and with the opposite sign of derivative for the parallel and perpendicular transitions. Altogether, one can conclude that there is no one striking feature which distinguishes these two systems and can thus explain the significantly different \( \Gamma^* \) quantum yield values observed.

As the present calculation clearly show, the \( \text{A} \) band in CH\textsubscript{3}I is dominated by the \( 3\text{Q}_0^*→\tilde{X} \) transition. Lowering of the molecular symmetry to \( \text{C}_r \) or \( \text{C}_1 \), e.g., bending, can only lead to stronger nonadiabatic (radial) coupling of the \( 3\text{Q}_0^* \) and \( \text{Q} \) states, to the enhancement of the nonadiabatic transitions between these two states, and, as a consequence, to a decrease of the \( \Gamma^* \) quantum yields. Therefore, the polyatomic character of the CH\textsubscript{3}I molecule and nonadiabatic coupling cannot be responsible for this effect as well.

From the above arguments, it is clear that the higher \( \Gamma^*/\Gamma \) branching ratios in CH\textsubscript{3}I in comparison with HI are caused by the enhancement of the parallel \( 3\text{Q}_0^*→\tilde{X} \) transition in the former system. This, in turn, is caused by significant changes in the electron density distribution when the H atom is substituted by the CH\textsubscript{3} radical. As discussed in Sec. III, there are two main contributions to the \( 3\text{Q}_0^*→\tilde{X} \) transition moment which are important at all C–I distances. The first one comes from the direct spin-orbit mixing of the \( 3\text{Q}_0^* \) and \( \tilde{X} \) states, and it is proportional to the dipole moment difference for the ground \( \text{A}_1 \) and \( 3\text{Q}(E) \) \( \Lambda\text{–S} \) states. As can be seen in Table V, this difference becomes notably larger in the CH\textsubscript{3}I molecule as compared to HI due to the fact that the outer \( \sigma^* \) electron is much more strongly shifted from the I atom in this case. This is characteristic for the equilibrium geometries of the systems discussed and particularly for somewhat larger C–I separations (3.6a\textsubscript{0} in HI and 4.75a\textsubscript{0} in CH\textsubscript{3}I) for which the \( \mu(3\text{Q}_0^*→\tilde{X}) \) maxima are reached.

The second important contribution to \( \mu(3\text{Q}_0^*→\tilde{X}) \) originates from the \( 3\text{Q} \) mixing with the valence \( 2\text{A}_1 \) (\( \sigma \rightarrow \sigma^* \)) state. The \( \sigma^* \) orbital has much less antibonding character in CH\textsubscript{3}I as compared to HI, and this results in the 2\text{A}_1 notably lower excitation energy in the polyatomic molecule. This leads to a stronger SO mixing of the \( 3\text{Q} \) and 2\text{A}_1 states and thus to a notably larger corresponding contribution into the \( 3\text{Q}_0^*(\text{A}_1)→\tilde{X} \) \( \text{A}_1 \) transition. Summarizing, one can say that significant distinctions in the electron density distribution in the HI and CH\textsubscript{3}I molecules, particularly in the \( \sigma^* \) character and localization, lead to a decisive increase in the strength of the \( 3\text{Q}_0^*(\text{A}_1) \) channel excitation.

V. CONCLUSION

The LSC-SO-CI and MR-SO-CI approaches have been employed to calculate dipole and transition moments for the ground and low-lying excited states of the CH\textsubscript{3}I molecule and on this basis to obtain partial and total absorption spectrum of the \( \text{A} \) band and the \( \Phi_T(\nu) \) quantum yield as a function of excitation energy.

![Table of relevant absorption properties of HI and CH\textsubscript{3}I.](image)
Similar to the HI case analyzed in our earlier study,\textsuperscript{32} the calculated $^3Q_{0^+}$, $^3Q_{1^+}$, and $^1Q\leftarrow\tilde{X}$ transition moments show a strong dependence on the C–I distance in the FC region, which is opposite for the parallel and perpendicular transitions. This makes the assumption of constant values for these quantities, which is usually employed for obtaining the corresponding potentials from experimental data and modeling the A-band partial contributions, a poor approximation.

Test CI calculations carried out at smaller selection thresholds indicate that the $\mu(^1Q\leftarrow\tilde{X}^1A_1)$ values are very sensitive to the sizes of CI spaces considered and that a fairly high level of CI treatment is needed to achieve proper convergence. Spin-orbit interaction is also important in this respect, producing a redistribution of absorption probability between transitions to the $^3Q_{1^+}$ and $^3Q_{0^+}$ states and thus influencing the total absorption curve as well as the I band yields. It has also been found that in order to obtain accurate dipole moment values for the $^3Q_{0^+}\leftarrow\tilde{X}A_1$ transition, it is necessary to include SO coupling with the higher-lying valence and Rydberg states of $^1A_1$ and $^3E$ symmetries. A consideration of the SO interaction only within the A-band manifold and with the ground state leads to a strong underestimation of this quantity.

The calculated total absorption spectrum agrees fairly well with the experimental data. A shift of the $^1Q$ potential by 900 cm$^{-1}$ to lower energies removes a slight shoulder on the high-energy side of the total absorption curve and improves the agreement with experiment in the middle of the band. An additional small shift of the total spectrum downward by 200 cm$^{-1}$ due to the influence of the spectator vibrations further improves this agreement.

On the basis of the calculated absorption data, the I$^+$ quantum yield has been determined as a function of excitation energy. The $\Phi(T)(v)$ values thus obtained are in good overall agreement with the measured data. It is shown that the strong dependence of the relevant transition moments on the C–I distance opens a possibility for vibrational state control of the final photodissociation products. It is demonstrated that $\Phi(T)(v)$ quantum yields up to 0.9 can be achieved when vibrationally hot CH$_3$I molecules ($v''=1,2$) are excited in the ($32-35$)×10$^3$ cm$^{-1}$ spectral range. The above effect also reveals itself in a strong temperature dependence of the $\Phi(T)(v)$ values, particularly in the low-energy part of the A band, bringing them in much better agreement with the experimental data.

It is important to emphasize that vibrational state control of the I$^+/I$ branching ratio in the alkyl-(hydrogen) iodide photodissociation has an electronic rather than a dynamic nature. Due to a different electron density distribution at various molecular geometries, one achieves more efficient excitation of a particular fragmentation channel rather than influences the dynamics of the decay process. This result has obvious and strong consequences. For example, photoexcitation of the vibrationally hot CH$_3$I molecules in the above energy range provides a good possibility for obtaining more efficient laser generation at the atomic I($^2P_{1/2}$)→I($^2P_{3/2}$) transition.

We would like to underline that although theoretical analysis of multichannel photodissociation has become quite popular in the last years, it is concentrated as a rule on the energetic part of the problem and does not include \textit{ab initio} calculations of transition moments as functions of geometry and partial absorption spectra for various dissociation channels. The present study is a rare if not a unique example, particularly for molecules with heavy atoms, where such calculations are carried out, and it shows which strong consequences relatively small effects in the absorption process may have on the yields of the final products.

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