Photoelectron spectroscopic study of the E#e Jahn–Teller effect in the presence of a tunable spin–orbit interaction. I. Photoionization dynamics of methyl iodide and rotational fine structure of CH₃I⁺ and CD₃I⁺

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Photoelectron spectroscopic study of the $E \otimes e$ Jahn–Teller effect in the presence of a tunable spin–orbit interaction. I. Photoionization dynamics of methyl iodide and rotational fine structure of CH_3I^+ and CD_3I^+

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The high-resolution single-photon pulsed-field-ionization zero-kinetic-energy photoelectron spectra of the $\tilde{X}^+ \ ^2E_{3/2} \leftarrow \tilde{X} \ ^1A_1$ transition of CH_3I and CD_3I have been recorded. The spectral resolution of better than 0.15 cm^{-1} enabled the observation of the rotational structure. CH_3I^+ and CD_3I^+ are subject to a weak $E \otimes e$ Jahn–Teller effect and strong spin–orbit coupling. The treatment of the rovibronic structure of the photoelectron spectra in the corresponding spin double group, $C_{3v}^2(M)$, including the effects of the spin–orbit interaction and the vibrational angular momentum, allowed the reproduction of the experimentally observed transitions with spectroscopic accuracy. The relevant spin–orbit and linear Jahn–Teller coupling parameters of the $\tilde{X}^+$ ground state were derived from the analysis of the spectra of the two isotopomers, and improved values were obtained for the adiabatic ionization energies [$E_1(\text{CH}_3\text{I})/hc = 76931.35(20) \text{ cm}^{-1}$ and $E_1(\text{CD}_3\text{I})/hc = 76957.40(20) \text{ cm}^{-1}$] and the rotational constants of the cations. Rovibronic photoionization selection rules were derived for transitions connecting neutral states following Hund’s-case-(b)-type angular momentum coupling and ionic states following Hund’s-case-(a)-type coupling. The selection rules, expressed in terms of the angular momentum projection quantum number P , account for all observed transitions and provide an explanation for the nonobservation of several rotational sub-bands in the mass-analyzed threshold-ionization spectra of CH_3I and CD_3I reported recently by Lee *et al.* [J. Chem. Phys. **128**, 044310 (2008)]. © 2011 American Institute of Physics. [doi:10.1063/1.3547548]

I. INTRODUCTION

The structure and dynamics of molecules that are simultaneously subject to the Jahn–Teller effect and spin–orbit coupling strongly depend on the relative strength of different types of rovibronic interactions.^{1–3} The spectra of such molecules are complex, and the extraction of reliable sets of spectroscopic parameters represents a very interesting, but also challenging, task.

Cations of the methyl-halide family (CH_3X^+ , with $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{At}$) and the corresponding isoelectronic neutral molecules (CH_3Y , with $\text{Y} = \text{O}, \text{S}, \text{Se}, \text{Te}, \text{Po}$) are prototypical systems to study the Jahn–Teller effect and spin–orbit coupling. Because the strength of the spin–orbit coupling rapidly increases with the atomic number of X and Y , CH_3X^+ and CH_3Y molecules offer the possibility to investigate the Jahn–Teller effect as a function of the strength of the spin–orbit interaction. Comparison of the positively charged and neutral species also enables the study of subtle vibronic-coupling effects and may assist in gaining a global understanding of the combined effect of the $E \otimes e$ Jahn–Teller effect and spin–orbit coupling in these important classes of free radicals, and also in recognizing general trends relevant to the description of a wider range of molecular systems.

The spectroscopic data currently available on the methyl-halide cations have been obtained almost exclusively by photoelectron spectroscopy. He I and He II photoelectron

spectra have provided information on the vibronic structure of the $\tilde{X}^+ \ ^2E$ ground state^{4–11} from which the general features of the Jahn–Teller effect have been derived, including a qualitative understanding of the role of the spin–orbit coupling. Theoretical studies of the Jahn–Teller effect have been reported that account for the vibronic structure observed in these He I photoelectron spectra.^{12–14} Mass-analyzed threshold-ionization (MATI) and pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectra of the $\tilde{X}^+ \leftarrow \tilde{X}$ transitions of CH_3I , its fully deuterated isotopomer CD_3I , and CH_3Br with partial resolution of the rotational structure have also been recorded and analyzed,^{15–20} providing insights into the complex interplay of vibronic, spin–orbit, and rotational effects in Jahn–Teller-coupled systems.

Of particular interest is the observation, by Kim and his co-workers,²⁰ of “satellite” bands in the MATI spectrum of the origin band of the $\tilde{X}^+ \leftarrow \tilde{X}$ photoionizing transition of CH_3I and CD_3I . In their analysis, Kim and co-workers could account for the positions of these satellite bands as resulting from the K -branch structure by carrying out an analysis of the $E \otimes e$ Jahn–Teller effect and spin–orbit coupling in the $\tilde{X}^+$ state of CH_3I^+ and CD_3I^+ . When comparing the observed satellite bands, classified in terms of changes $\Delta K = K^+ - K$ (K^+ and K are the quantum numbers for the projection of the total angular momentum excluding spin onto the three-fold symmetry axis of the cationic and neutral species, respectively), with the predictions from general rovibronic symmetry selection rules, they made the observations²⁰ that “ $v_{|K|}^{K^+} = 0_2^{-3}$, 0_2^5 , and 0_1^{-4} transitions, even though allowed by

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symmetry, are absent in the spectrum” and that “a clear-cut explanation for their absence has not been presented yet” and may require “rigorous calculation of the rotational line intensities by using advanced theories such as an improved spectator model.” They also suggested that “high resolution ZEKE or MATI-PD studies, not only for the 0-0 band but also for the fundamentals and overtones, will be needed to determine the K^+ composition of each band.”²⁰

Following earlier work by Morrison and co-workers^{21–23} on the photodissociation spectrum of CH_3I^+ and CD_3I^+ , Kim and his co-workers^{24–26} have also recorded high-resolution spectra of the $\tilde{A}^+ \leftarrow \tilde{X}^+$ band system of CH_3I^+ and CD_3I^+ by using a combination of mass-analyzed threshold ionization spectroscopy to prepare selected rotational levels of the cations and photodissociation spectroscopy to probe the $\tilde{A}^+ \leftarrow \tilde{X}^+$ transition with high sensitivity and spectral resolution. Combining these results with those obtained in their MATI study,²⁰ they could derive the molecular parameters determining the structure of both CH_3I^+ and CD_3I^+ .²⁶

Despite these studies, the rovibronic structures of the methyl-halide cations remain less well characterized and understood than is the case for the corresponding isoelectronic neutral molecules CH_3O and CH_3S , for which high-resolution spectra have been obtained and analyzed.^{3,27–30} The methoxy radical, in particular, has served as a prototypical molecule to study the Jahn–Teller effect and spin–orbit coupling, and represents one of the best understood molecular systems subject to the $E \otimes e$ Jahn–Teller effect (see Refs. 3, 27, 29, and 30 and references therein).

This article is the first of a series of articles presenting the results of a high-resolution photoelectron spectroscopic study of the combined Jahn–Teller and spin–orbit interactions in the methyl-halide cations. It describes the measurement and analysis of high-resolution (0.15 cm^{-1}) PFI-ZEKE photoelectron spectra of the vibronic ${}^2E_{3/2}$ ground state of CH_3I^+ and CD_3I^+ . The analysis of the rotational structure is based on an effective Hamiltonian derived by Brown³¹ in the spin double group $C_{3v}^2(M)$, and on photoionization selection rules that account for the change from a Hund’s-case-(b)-type to a Hund’s-case-(a)-type angular momentum coupling resulting from ionization. The emphasis of the present article is placed on the explanation of the satellite bands observed in the photoelectron spectra of CH_3I and CD_3I in terms of a rigorous model of the photoionization dynamics, largely motivated by the previous work of Kim and co-workers²⁰ mentioned above.

To anticipate the main results presented in this article, Figs. 1(a) and 1(b) show survey spectra of the origin bands of the PFI-ZEKE photoelectron spectra of the $\tilde{X}^+ {}^2E_{3/2} \leftarrow \tilde{X}^1A_1$ transitions of CH_3I and CD_3I , respectively. These spectra consist each of a strong band and of several weaker satellite bands on the high-wavenumber side first observed by Kim and co-workers (see above). The figure contains assignments of the satellite bands in terms of ΔK sub-bands as proposed by Kim and co-workers²⁰ (upper assignment bars in Fig. 1) with the nonobserved transitions indicated by dashed lines. In order to find a complete explanation for the presence and absence of specific satellite bands, the rovibronic photoionization selection rule $\Delta P = P^+ - K = \pm 3/2$ was derived in the spin double group using the quantum numbers

$P = K + \Sigma$, $j = \ell_v + \frac{1}{2}\Lambda$,³² and $\Omega' = \Lambda - \ell_v + \Sigma$ (Ref. 3) for transitions to the lower $E_{3/2}$ spin–orbit component. This selection rule, which led to the lower assignment bars in Fig. 1, does not only account for the transitions observed by Kim and co-workers²⁰ and in our new spectra, but also predicts that the nonobserved ΔK satellite bands are forbidden.

In subsequent articles of this series,³³ the formalism derived here to treat the rovibronic structure of the photoelectron spectrum of methyl iodide will be applied to the photoelectron spectra of the $\tilde{X}^+ \leftarrow \tilde{X}$ ionizing transitions of CH_3Cl and CH_3F .

II. EXPERIMENT

The rotationally resolved PFI-ZEKE photoelectron spectra of the origin bands of the $\tilde{X}^+ {}^2E_{3/2} \leftarrow \tilde{X}^1A_1$ transitions of CH_3I and CD_3I were recorded using a vacuum-ultraviolet (VUV) laser source with a bandwidth of 0.008 cm^{-1} (Ref. 34) and a photoelectron spectrometer described in Ref. 35. Tunable VUV radiation in the range $\tilde{\nu}_{\text{VUV}} = 76920\text{--}77000\text{ cm}^{-1}$ was generated by coherent four-wave difference-frequency mixing ($\tilde{\nu}_{\text{VUV}} = 2\tilde{\nu}_1 - \tilde{\nu}_2$) in a krypton gas cell using two pulse-amplified single-mode ring dye lasers. The output of the first ring dye laser was amplified in a series of three Nd:YAG-pumped dye cells, and frequency-tripled in two sequential β -barium-borate crystals. The fundamental frequency was locked to an I_2 line, so that the tripled frequency corresponded to the $(4p)^6 \rightarrow (4p)^5 5p[1/2]_0$ two-photon transition in atomic krypton at $2\tilde{\nu}_1 = 94092.9\text{ cm}^{-1}$, as explained in Ref. 36. The tunable output $\tilde{\nu}_2$ of a second ring dye laser was also pulse amplified in three stages, using Sulforhodamine B as an amplification dye. Its wave number was calibrated to a precision of better than 0.02 cm^{-1} by recording, with each spectrum, the laser-induced fluorescence spectrum of I_2 .

CD_3I (purity 99.6%, isotope purity $> 99\%$) was synthesized from CD_3OD following the method described in Ref. 37. Gas mixtures of $\sim 10\%$ CH_3I (Aldrich, purity 99.9%) or CD_3I in argon at a stagnation pressure of 2 bar were introduced into the experimental chambers through a pulsed valve and a skimmer. The molecules in the resulting supersonic beam, with a rotational temperature of $\approx 10\text{ K}$, were subsequently excited by the VUV radiation to high Rydberg states ($n > 250$) located below the rovibronic ionization thresholds. The excited Rydberg states were field-ionized by sequences of electric-field pulses and the resulting electron current recorded as a function of the wave number $\tilde{\nu}_2$.

To obtain a resolution sufficient to observe the rotational fine structure of the photoelectron spectra of CH_3I and CD_3I , multipulse electric-field sequences were applied $2\text{ }\mu\text{s}$ after the VUV light pulses. These sequences consisted of a $+166\text{ mVcm}^{-1}$ discrimination pulse of $1\text{ }\mu\text{s}$ duration followed by several field-ionization (and extraction) pulses of 200 ns duration and gradually decreasing strengths, as explained in Ref. 35. Steps of either -33 , -17 , or -8 mVcm^{-1} were used between adjacent pulses, starting with a pulse strength of -83 mVcm^{-1} . The optimal compromise between high resolution and high signal-to-noise ratio was found at a

FIG. 1. Overview of the PFI-ZEKE photoelectron spectra of the $\tilde{X}^+ 2E_{3/2} \leftarrow \tilde{X} 1A_1$ transitions of (a) CH_3I and (b) CD_3I . In each panel, the upper assignments are taken from Ref. 20, and the lower result from the present analysis. See text for details.

step size of -17 mVcm^{-1} , resulting in a full width at half maximum (FWHM) of 0.15 cm^{-1} for all spectra except the weakest ones, which were recorded using a step size of -33 mVcm^{-1} (FWHM of 0.25 cm^{-1}). The positions of the field-free ionization thresholds were obtained by correcting for the field-induced shift of the ionization thresholds following the procedure described in Ref. 35. The absolute uncertainty in the determination of the ionization thresholds is estimated to be 0.2 cm^{-1} . The relative positions of the thresholds corresponding to the different lines of the PFI-ZEKE photoelectron spectra can be determined with higher precision, typically 0.05 cm^{-1} or better, limited by the FWHM of the lines and the signal-to-noise ratio.

III. THEORETICAL BACKGROUND

CX_3Y molecules are in general of $C_{3v}(M)$ symmetry. In the ground state, CH_3I and CD_3I have the electronic config-

uration $[\dots](e)^4(a_1)^2(e)^4$,⁸ where the inner-shell orbitals are indicated as $[\dots]$. Consequently, their ground electronic state is totally symmetric with zero electron spin ($\tilde{X} 1A_1$). The ground state of the cation has the configuration $[\dots](e)^4(a_1)^2(e)^3$, is designated $\tilde{X}^+ 2E$ in $C_{3v}(M)$, and is subject to a $E \otimes e$ Jahn–Teller effect.³² The outermost orbital (e) has significant contributions from the lone pair of the I atom so that the Jahn–Teller effect is accompanied by a strong spin–orbit interaction. The formalism needed to simultaneously describe the linear $E \otimes e$ Jahn–Teller effect and spin–orbit coupling in the $C_{3v}(M)$ molecular symmetry group has been presented in Ref. 3. The $E \otimes e$ Jahn–Teller effect leads to a distortion of the geometry of the E ground state along a vibrational mode of e symmetry to C_s equilibrium structures. When the quadratic Jahn–Teller effect is negligible and only the linear Jahn–Teller effect needs to be considered, there is an infinite number of equally distorted minima at the bottom of a circular trough around the conical intersection of C_{3v}

geometry. The molecular motion along the trough, called pseudorotation, is then free. A quadratic Jahn–Teller effect leads to the formation of three minima along the circular trough separated by potential barriers, and to a hindered pseudorotation.¹

The linear Jahn–Teller stabilization energy E_{JT} corresponds to the sum of contributions from all active e vibrational modes

$$E_{JT} = \sum_i E_{JT,i} = \sum_i \omega_i D_i, \quad (1)$$

where the parameter D_i is used to quantify the linear Jahn–Teller coupling strength of mode i with harmonic frequency ω_i . If $D_i \ll 1$ (or $E_{JT,i} \ll \omega_i$) for all i , the zero-point energy exceeds the stabilization energy and a purely dynamical Jahn–Teller effect results. The spin–orbit interaction complicates the situation, introduces additional splittings, and its treatment necessitates the use of spin double groups, as will be explained below (see also Refs. 3 and 38).

CH_3I^+ and CD_3I^+ are molecules that are subject to a weak linear Jahn–Teller effect and strong spin–orbit coupling. The $\tilde{X}^+ {}^2\text{E}$ state, therefore, splits into two distinct components $\text{E}_{1/2}$ and $\text{E}_{3/2}$. The present work is restricted to the lower spin–orbit component ($\text{E}_{3/2}$) of the vibronic ground state of CH_3I^+ and CD_3I^+ .

A. Vibronic and spin–orbit coupling in the ${}^2\text{E}$ electronic ground state

The $\text{E} \otimes e$ Jahn–Teller effect in a ${}^2\text{E}$ electronic state can be regarded as arising from the coupling of the vibrational $|v, \ell_v\rangle$ (v and ℓ_v are the vibrational and angular momentum quantum numbers of the degenerate e mode) and electronic $|\Lambda\rangle$ (Λ is the quantum number describing the projection of the electronic orbital angular momentum onto the C_3 axis) motions, resulting in the necessity to introduce a new conserved Jahn–Teller quantum number $j = \ell_v + \frac{1}{2}\Lambda$ to describe the vibronic eigenfunctions and their angular dependence with respect to rotations about the z axis of the molecule-fixed coordinate system.³² The electronic orbital angular momentum $|\Lambda\rangle$ is also coupled to the electron spin $|S = 1/2, \Sigma\rangle$ by the spin–orbit interaction, which can be described by the effective spin–orbit coupling operator

$$\frac{\hat{H}_{\text{SO}}}{hc} = \frac{a}{\hbar^2} \hat{L} \cdot \hat{S}, \quad (2)$$

where a represents the spin–orbit coupling constant of the molecule in wave number units. In the methyl halide cations, $a < 0$.⁸ As shown by Hougen,³⁹ the off-diagonal terms in the spin–orbit Hamiltonian of Eq. (2) vanish in the absence of interactions with other electronic states in a molecule of C_{3v} symmetry. The A component of the effective P state (corresponding to the $\sigma_{\text{C-I}}$ bonding orbital) leads to an excited electronic state ($\tilde{A}^+ {}^2\text{A}_1$) located 2.65 eV above the $\tilde{X}^+ {}^2\text{E}$ ground state.⁴ This separation is much larger than the spin–orbit splitting, so that one can assume in good approximation that

$$\frac{\hbar^2}{hc} \hat{H}_{\text{SO}} = a \hat{L} \cdot \hat{S} \cong a \hat{L}_z \hat{S}_z \quad (3)$$

and

$$\frac{\hbar^2}{hc} \hat{H}_{\text{SO}} |j, \Sigma\rangle = a \zeta_e d \Sigma |j, \Sigma\rangle, \quad (4)$$

where ζ_e represents a reduction factor of the coupling of the electronic orbital angular momentum onto the molecular z axis in nonlinear polyatomic molecules and d is an additional reduction of the observable spin–orbit splitting resulting from the Jahn–Teller effect.⁴⁰ ζ_e has been interpreted as a general reduction of the effect of the spin–orbit coupling strength caused by the off-axis atoms (and their electrons) in nonlinear molecules.^{41,42} It is also referred to as the electronic expectation value, $\langle \Lambda = \pm 1 | \hat{L}_z | \Lambda = \pm 1 \rangle = \pm \zeta_e$, where $\Lambda = \pm 1$ represents the two components of the degenerate electronic E state.³¹ In the last part of this article series,³³ we shall exploit the comparison of the Jahn–Teller effect in the ground ${}^2\text{E}$ states of CH_3F^+ , CH_3O , CH_3Cl^+ , CH_3S , and CH_3I^+ to provide a simple physical interpretation of ζ_e . In CH_3I^+ and CD_3I^+ , the overall energy level structure is dominated by an almost “atomic” spin–orbit interaction of the I atom, and ζ_e is found to be close to unity, as shown below in Sec. IV.

The vibronic and spin–orbit interactions are conveniently expressed in matrix form using the basis $|j, \ell_v, \Lambda, \Sigma\rangle$.³ Each spin–vibronic eigenstate has an intrinsic double (Kramers) degeneracy resulting from the half-integer total angular momentum quantum number.⁴³ The matrix elements involving basis functions of the form $|+j, +\ell_v, +\Lambda, +\Sigma\rangle$ and $|-j, -\ell_v, -\Lambda, -\Sigma\rangle$ are equivalent, so that one can restrict the treatment to basis functions with $j > 0$. Because the Jahn–Teller coupling strength is weak in CH_3I^+ and CD_3I^+ ,^{12,20} the $\text{E}_{3/2}$ vibronic ground state possesses mainly $|1/2, 0, 1, 1/2\rangle$ character, with a weaker vibronically induced contribution of $|1/2, 1, -1, 1/2\rangle$ character,³ and can be represented by

$$|\tilde{X}^+ {}^2\text{E}_{3/2}\rangle = a_{3/2} |1/2, 0, 1, 1/2\rangle + b_{3/2} |1/2, 1, -1, 1/2\rangle$$

with $|a_{3/2}| > |b_{3/2}|$. (5)

Similarly, the $\tilde{X}^+ {}^2\text{E}_{1/2}$ state is described by

$$|\tilde{X}^+ {}^2\text{E}_{1/2}\rangle = a_{1/2} |1/2, 0, 1, -1/2\rangle + b_{1/2} |1/2, 1, -1, -1/2\rangle$$

with $|a_{1/2}| > |b_{1/2}|$. (6)

The symmetry of the spin–vibronic basis functions can be determined by introducing a projection quantum number³

$$\Omega' = \Lambda - \ell_v + \Sigma, \quad (7)$$

where states with $\Omega' = 3n \pm 3/2$ and $3n \pm 1/2$ (n integer) are of $\text{E}_{3/2}$ and $\text{E}_{1/2}$ symmetry in $\text{C}_{3v}^2(\text{M})$, respectively. In the definition of Ω' , the projection of the vibrational angular momentum quantum number ℓ_v enters Eq. (7) with a negative sign, which is a result of the sense of rotation in the molecule-fixed reference frame, as commonly defined for $|v, \ell_v\rangle$. Ω' can, therefore, be regarded as the quantum number associated with the projection of the spin–vibronic angular momenta onto the molecule-fixed z axis, i.e., $\Omega' = P - K_{\text{rot}}$, where P and K_{rot} are the projection quantum numbers of the total angular momentum $\vec{J}$ and the rotational angular momentum $\vec{R}$, respectively. Therefore, in the ${}^2\text{E}_{3/2}$ ground state of CH_3I^+ and CD_3I^+ , the dominant $|+1/2, 0, +1, +1/2\rangle$ contribution to the total wavefunction in Eq. (5) has $\Omega' = +3/2$, and

the weaker $|+1/2, +1, -1, +1/2\rangle$ contribution has $\Omega' = -1 - 1 + 1/2 = -3/2$.

The strong coupling of the unpaired electron spin onto the molecular z axis requires the use of the spin double group $C_{3v}^2(M)$, which contains an additional symmetry operation R corresponding to a 2π rotation that changes the sign of all wavefunctions corresponding to double-valued representations [i.e., $E_{1/2}$ and $E_{3/2}$ in $C_{3v}^2(M)$].⁴⁴ In $E_{1/2}$ and $E_{3/2}$ representations, the identity corresponds to a rotation by 4π ($R^2 = E$). Consequently, the symmetry operation R allows the distinction between the two components of each pair of degenerate molecular states. Single-valued representations [i.e., A_1 , A_2 , and E in $C_{3v}(M)$] are characterized by $R = E$, and, therefore, also appear in the original $C_{3v}(M)$ symmetry group. The ground electronic state of CH_3I^+ has to be described in the $C_{3v}^2(M)$ group to include the effects of the electron spin. The representation of an $S = 1/2$ spin function Γ_{spin}^+ is $E_{1/2}$, so that the spin-vibronic wavefunctions have symmetry $\Gamma_{\text{ves}}^+ = \Gamma_{\text{ve}}^+ \otimes \Gamma_{\text{spin}}^+ = E \otimes E_{1/2} = E_{3/2} \oplus E_{1/2}$. As $a < 0$, the spin-vibronic ground state of CH_3I^+ is of $E_{3/2}$ symmetry.

B. Rotational fine structure

The pure rotational Hamiltonian of a polyatomic molecule is^{45,46}

$$\hbar^2 \hat{H}_{\text{rot}} = \frac{1}{2} \sum_{\alpha\beta} (\hat{N}_\alpha - \hat{\pi}_\alpha) \mu_{\alpha\beta} (\hat{N}_\beta - \hat{\pi}_\beta), \quad (8)$$

where $\mu_{\alpha\beta}$ ($\alpha, \beta = x, y, z$) stands for an element of an effective reciprocal inertial tensor, $\hat{N} = \hat{J} - \hat{S}$ represents the total angular momentum excluding spin, and $\hat{\pi}$ is the vibronic (internal) angular momentum, i.e., the sum of the electronic orbital and the vibrational angular momentum. In a molecule of $C_{3v}(M)$ symmetry in a degenerate vibronic 2E state, none of these angular momenta is equal to zero. When the coupling of the electron spin to the internuclear z axis is strong, the angular momentum coupling is commonly referred to as Hund's-case-(a) coupling although Hund's classification was introduced for diatomic molecules.⁴⁷ In a Hund's-case-(a)-coupled polyatomic molecule, the rotational motion ($\hat{H}_{\text{rot}}$) and the spin–orbit coupling ($\hat{H}_{\text{SO}}$) have to be treated together, resulting in the effective Hamiltonian

$$\begin{aligned} \frac{\hbar^2}{hc} [\hat{H}_{\text{rot}} + \hat{H}_{\text{SO}}] = & B(\hat{J} - \hat{S} - \hat{\pi})^2 \\ & + (A - B)(\hat{J}_z - \hat{S}_z - \hat{\pi}_z)^2 + a\hat{L}_z\hat{S}_z \end{aligned} \quad (9)$$

for a prolate symmetric-top molecule, where A and B are the rotational constants (in cm^{-1}) along the principal axes of the molecule. The analysis of the rotational structure of the PFI-ZEKE photoelectron spectra of CH_3I and CD_3I does not necessitate all terms of the full expansion of the Hamiltonian. The approximations to Eq. (9) introduced by Brown³¹ are adopted here, resulting in the following effective rotation-spin–orbit Hamiltonian $\hat{H}_{\text{RSO}} \cong \hat{H}_{\text{rot}} + \hat{H}_{\text{SO}}$ for a molecule described by Hund's-case-(a)-type angular

momentum coupling:

$$\frac{\hbar^2}{hc} \hat{H}_{\text{RSO}} = B\hat{J}^2 + (A - B)\hat{J}_z^2 \quad (10a)$$

$$-2A\hat{J}_z\hat{\pi}_z + A\hat{\pi}_z^2 \quad (10b)$$

$$\begin{aligned} & -2A\hat{J}_z\hat{S}_z + 2A\hat{S}_z\hat{\pi}_z + B\hat{S}^2 \\ & + (A - B)\hat{S}_z^2 + a\hat{L}_z\hat{S}_z \end{aligned} \quad (10c)$$

$$-B(\hat{J}_+\hat{S}_- + \hat{J}_-\hat{S}_+). \quad (10d)$$

The projection $\hat{\pi}_z$ of the vibronic angular momentum onto the molecular z axis, when only one Jahn–Teller-active mode t is considered, results in^{31,48}

$$\begin{aligned} \hat{\pi}_z|j\rangle &= \left(\zeta_{t_1,t_2}j + \zeta_e d - \frac{1}{2}\zeta_{t_1,t_2}d + \sum_{t'} \zeta_{t',t'_2}\ell_{t'} \right) |j\rangle \\ &= \zeta_{\text{ev}}|j\rangle, \end{aligned} \quad (11)$$

where ζ_e and d have already been introduced in Eq. (4) to describe the reduction of the observable spin–orbit splitting. The terms containing ζ_{t_1,t_2} and ζ_{t',t'_2} describe the Coriolis coupling of the two components (t_1 and t_2) of the Jahn–Teller active mode and the coupling to the other degenerate e modes $t' \neq t$, respectively. ζ_{ev} is an effective vibronic Coriolis coupling term, which, for the vibronic ground state considered here ($j = +1/2$), can be expressed as

$$\zeta_{\text{ev}} = \zeta_e d + \frac{1}{2}\zeta_{t_1,t_2}(1 - d). \quad (12)$$

Choosing linear combinations of the rotation-spin-vibronic basis functions having a well-defined parity²⁷

$$\begin{aligned} & \frac{1}{\sqrt{2}}(|j = +1/2, \Sigma\rangle|J, +P, M_J\rangle \\ & \pm (-1)^{J-P+1/2-\Sigma}|j = -1/2, -\Sigma\rangle|J, -P, M_J\rangle) \end{aligned} \quad (13)$$

allows a reduction of the size of the matrix $\hat{H}_{\text{RSO}}$ by a factor of 2. In Eq. (13), J is the total angular momentum, and P and M_J are the quantum numbers associated with its projections on the molecular and the space-fixed z axis, respectively. P is related to the projection K of the total angular momentum excluding spin $\hat{N} = \hat{J} - \hat{S}$ by

$$P = K + \Sigma \quad (= \Omega' + K_{\text{rot}}). \quad (14)$$

Because expectation values of $\hat{H}_{\text{RSO}}$ with respect to the functions

$$|+j, +\Sigma, J, +P\rangle \quad (15)$$

and

$$|-j, -\Sigma, J, -P\rangle \quad (16)$$

are equal, any of the three sets of basis functions [Eqs. (13) (15), and (16)] can be chosen to determine the energy spectrum. The diagonal part of $\hat{H}_{\text{RSO}}$ consists of terms describing a rigid-rotor [Eq. (10a)], the influence of

the vibronic Jahn–Teller coupling on the rotational structure [Eq. (10b)], and several spin and spin–orbit dependent terms [Eq. (10c)]. Neglecting the spin-uncoupling term [Eq. (10d)], the eigenvalues of $\hat{H}_{\text{RSO}}$ have the form

$$\frac{E_{\text{RSO}}}{hc} = BJ(J+1) + (A-B)P^2 \quad (17a)$$

$$-2AP\zeta_{\text{ev}} + A\zeta_{\text{ev}}^2 \quad (17b)$$

$$-2AP\Sigma + 2A\Sigma\zeta_{\text{ev}} + \frac{B}{2} + \frac{A}{4} + a\zeta_{\text{ev}}d\Sigma. \quad (17c)$$

Because of the anomalous commutation relations for molecule-fixed rotational angular momenta,^{46,49} the off-diagonal elements of the form $-B(\hat{J}_+\hat{S}_- + \hat{J}_-\hat{S}_+)$ in Eq. (10d) lead to either an increase or a decrease in both P and Σ . Consequently, $\hat{H}_{\text{RSO}}$ has a block-diagonal form with 2×2 blocks corresponding to the basis functions $|+j, \Sigma = -1/2, J, P\rangle$ and $|+j, \Sigma = +1/2, J, P+1\rangle$.³¹ With the use of Eq. (14), one can see that each of these 2×2 blocks has a well-defined value of K :

$$K = P - (-1/2) = P + 1 - 1/2, \quad (18)$$

so that K is a good quantum number of $\hat{H}_{\text{RSO}}$. In contrast, P is strictly a good quantum number only in the Hund's-case-(a) limit where the contribution from Eq. (10d) is much smaller than $a\zeta_{\text{ev}}d$.³¹

The total angular momentum quantum number is half-integer, and the rovibronic symmetry has to be derived in the spin double group $C_{3v}^2(M)$, as was done for the spin-vibronic states in Sec. III A. The symmetry of the total wavefunction, $\Gamma_{\text{rves}} = \Gamma_{\text{ves}} \otimes \Gamma_{\text{r}}$, must correspond to a single-valued representation of the $C_{3v}^2(M)$ spin double group, i.e., it must also be a representation of $C_{3v}(M)$. However, the intrinsic double degeneracy of the spin-rovibronic states remains as long as no external fields are applied.

In all calculations of the PFI-ZEKE photoelectron spectra of CH_3I and CD_3I presented in Sec. IV, the rovibronic energy levels of the cation were determined by calculating the eigenvalues of the effective Hamiltonian $\hat{H}_{\text{RSO}}$ given in Eq. (10).

C. Rotational energy levels in a Hund's-case-(a)-coupled molecule

Figure 2 shows an energy diagram of the rotational states of the $\tilde{X}^+ 2E_{3/2}$ ground state of CH_3I^+ with $J^+ \leq 7/2$ calculated with the molecular parameters derived from the spectroscopic analysis presented in Sec. IV (Table II), except for ζ_{ev} , which was varied from 0.1 to 1.0. The rotational structure in Fig. 2 is drawn relative to the origin of the $2E_{3/2}$ band, i.e., the term $a\zeta_{\text{ev}}d\Lambda\Sigma$, though nonzero, has been disregarded. The reason for starting the correlation diagram at the value of 0.1 for ζ_{ev} is that, below this value, the two spin-orbit components become so closely spaced that the coupling situation evolves toward Hund's-case-(b)-type coupling, and the treatment of the rotational structure necessitates the consideration of both spin-orbit components.

FIG. 2. Rotational energy levels $|\Sigma^+ = +1/2, J^+, P^+\rangle$ of a Hund's-case-(a)-coupled symmetric-top molecule in the $2E_{3/2}$ vibronic ground state. The rotational constants A^+ and B^+ used in the calculations are those summarized in Table II for the $\tilde{X}^+ 2E_{3/2}$ ground state of CH_3I^+ . The dependence of the rotational energies on the effective vibronic Coriolis coupling parameter ζ_{ev} of the states with $J^+ = 1/2 - 7/2$ is shown as solid ($J^+ = 1/2$), dashed ($J^+ = 3/2$), dashed-dotted ($J^+ = 5/2$), and dotted ($J^+ = 7/2$) lines. The vertical line ($\zeta_{\text{ev}} = 0.9755$) corresponds to the situation encountered in the $\tilde{X}^+ 2E_{3/2}$ ground state of CH_3I^+ .

In contrast to the situation encountered in $2\Pi_{3/2}$ states of Hund's-case-(a)-coupled diatomic molecules, where $J^+ \geq 3/2$, states with $J^+ = 1/2$ are observed in the $2E_{3/2}$ state ($|\Omega| = 3/2$) of a symmetric-top molecule, because the projection of the rotational angular momentum onto the molecular z axis can be nonzero in nonlinear molecules. The left-hand side of Fig. 2, with $\zeta_{\text{ev}} = 0.1$, corresponds to the energy level structure of a Hund's-case-(a)-type prolate symmetric-top molecule. The double degeneracy (i.e., $|N, \pm K\rangle$) of the rotational levels in the absence of strong coupling of the spin to the intermolecular axis is lifted by the spin-uncoupling interaction [Eq. (10d)] which has off-diagonal elements coupling the states $|\Sigma = -1/2\rangle|J^+, P^+\rangle$ and $|\Sigma = +1/2\rangle|J^+, P^+ + 1\rangle$. The increasing influence of the vibronic effects on the rotational structure that results from the increase of ζ_{ev} is observed as a near-linear dependence of the rotational energy levels on ζ_{ev} with a weak quadratic contribution from the second term of Eq. (17b). The influence of ζ_{ev} is most pronounced for states with $P^+ < 0$, which rapidly increase in energy because of the first terms in Eqs. (17b) and (17c). At large values of ζ_{ev} , these states form rovibronic satellite-band

structures on the high-energy side of the states with $P^+ > 0$, which tend to form a cluster of closely spaced levels at low energies. The energy-level structure corresponds closely to that observed in Fig. 1 and already briefly discussed in the Introduction, from which one can immediately conclude that ζ_{ev} is close to 1 in CH_3I^+ and CD_3I^+ . One can also conclude that the satellite-band structures represent a characteristic feature of the photoelectron spectra of CH_3I^+ and CD_3I^+ , and also of other ${}^2\text{E}$ molecules following Hund's coupling case (a). The calculations presented in Fig. 2 clearly indicate the spin-rovibronic origin of these satellite bands.

IV. PFI-ZEKE PHOTOELECTRON SPECTRA OF THE ORIGIN BAND OF THE $\tilde{X}^+ \leftarrow \tilde{X}$ TRANSITION OF CH_3I AND CD_3I AND DERIVATION OF MOLECULAR PARAMETERS

High-resolution PFI-ZEKE photoelectron spectra of the origin bands of the $\tilde{X}^+ {}^2\text{E}_{3/2} \leftarrow \tilde{X} {}^1\text{A}_1$ transitions of CH_3I and CD_3I are presented in Figs. 3 and 4, respectively. For clarity, the spectra are presented in two separate sets of panels, the left-hand side ones (a) showing the main band and the right-hand side ones (b) displaying the satellite bands on a magnified intensity scale. The analysis of the rotational structures of these spectra enabled the derivation of a full set of Jahn–Teller and spin–orbit coupling parameters and to classify the observed band structures in terms of the empirical selection rule $\Delta P = P^+ - K = \pm 3/2$, the main rotational band (left-hand side panels) corresponding to a superposition of five strong $\Delta P = +3/2$ sub-bands ($K = 0 \rightarrow P^+ = +3/2$, $K = +1 \rightarrow P^+ = +5/2$, $K = +2 \rightarrow P^+ = +7/2$, $K = -1 \rightarrow P^+ = +1/2$, and $K = -2 \rightarrow P^+ = -1/2$) and the weaker satellite bands (right-hand side panels) to $\Delta P = P^+ - K = -3/2$ sub-bands. The derivation of this selection rule based on theoretical considerations will be presented in Sec. V.

In Figs. 3 and 4, the top, bottom, and middle panels display the experimental spectra, calculated stick spectra, and their convolution with Gaussian line shape functions corresponding to the experimental resolution, respectively. Because the satellite bands are less congested than the main band, we have also provided the assignment of individual $|J, K\rangle \rightarrow |J^+, P^+\rangle$ transitions in Figs. 3(b) and 4(b), grouped in branches with $\Delta J = -5/2, -3/2, \dots, +5/2$. Weak $|\Delta J| = 7/2$ branches were also observed but are not labeled in the figures. The condition $J^+ \geq |P^+|$ implies that the $\Delta J = J^+ - J = +1/2, -1/2, -3/2, -5/2$, and $-7/2$ branches of the $K = 0 \rightarrow P^+ = -3/2$ satellite band are only observed for J values starting with 1, 2, 3, 4, and 5, respectively, and those of the $K = -1 \rightarrow P^+ = -5/2$ satellite band for J values starting with 2, 3, 4, 5, and 6.

Because the rotational constants of the neutral ground state are known,^{50–52} the rotational constant B^+ can readily be obtained from the spacings between the different ΔJ branches and from the positions of individual transitions to different J^+ levels within each ΔJ branch. As pointed out in Sec. III C, the energies of the rotational satellite bands depend on ζ_{ev} and A^+ , and, therefore, their analysis allowed the unambiguous determination of A^+ and ζ_{ev} . The adjust-

TABLE I. Empirically derived relative intensities of the different branches observed in the PFI-ZEKE photoelectron spectrum of the $\tilde{X}^+ {}^2\text{E}_{3/2} \leftarrow \tilde{X} {}^1\text{A}_1$ rotational transitions of CH_3I and CD_3I .

	CH_3I^+	CD_3I^+
$(\Delta J = 1/2) : (\Delta J = 3/2)$	1 : 3/5	1 : 1
$(\Delta J = 3/2) : (\Delta J = 5/2)$	1 : 2/3	1 : 2/3
$(\Delta J = 5/2) : (\Delta J = 7/2)$	1 : 1/4	1 : 1/4
$(\Delta J < 0) : (\Delta J > 0)$	1 : 1	1 : 2/3
$(\Delta P = +3/2) : (\Delta P = -3/2)$	1 : 1/6	1 : 1/6

ment of B^+ , A^+ , ζ_{ev} , and of the adiabatic ionization energy E_1 sufficed to satisfactorily reproduce the complete rovibronic structure shown in Figs. 3 and 4. The relative intensities of individual branches used in the calculations are summarized in Table I. On the low-energy side of the main rotational bands of the ${}^2\text{E}_{3/2}$ ground states [Figs. 3(a) and 4(a)], the intensities of the transitions are stronger than predicted by the calculations and this effect is more pronounced in CD_3I^+ than in CH_3I^+ . Ng and co-workers¹⁸ observed the same intensity behavior in their photoelectron spectroscopic study of CH_3I and interpreted it as arising from forced autoionization.⁵³

The molecular parameters obtained from our analysis are summarized in Tables II and III, where they are compared with earlier results. They indicate an R_0 structure of C_{3v} symmetry for both cations. As explained in Sec. III, a distortion to lower C_s symmetry caused by the Jahn–Teller effect is possible, but there is no indication of such a distortion in the experimental spectra, a conclusion also reached in Refs. 20 and 26. These results confirm the absence of a significant quadratic Jahn–Teller effect in the ground state of CH_3I^+ and CD_3I^+ .

The adiabatic ionization energies of $E_1/hc = 76931.35(20)$ and $76957.40(20) \text{ cm}^{-1}$ of CH_3I^+ and CD_3I^+ , respectively, are consistent with earlier experimental determinations, but are more precise. Overall, our spectroscopic parameters agree very well with the results reported by Kim and co-workers.^{20,25,26} The only exception concerns the rotational constant A^+ , which differs significantly both for CH_3I^+ and CD_3I^+ , and this discrepancy necessitates a discussion. Whereas the quantity $A^+\zeta_{\text{ev}}$ can be determined from the position of any given satellite band with respect to the main rotational band, individual values of A^+ and ζ_{ev} can only be derived from the positions of two or more satellite bands. Kim and his co-workers also observed the rotational satellite structures in CH_3I^+ and CD_3I^+ .²⁰ Their labeling of the cationic final states is consistent with the assignment presented here, under consideration of Eq. (14). Moreover, the transition wavenumbers reported in Ref. 20 for the $K = 0 \rightarrow K^+ = -2$ and $|K| = 1 \rightarrow K^+ = -3$ transitions agree with the results we obtained for the $K = 0 \rightarrow P^+ = -3/2$ and $K = -1 \rightarrow P^+ = -5/2$ transitions, respectively, within the respective experimental uncertainties. Consequently, the values $A^+\zeta_{\text{ev}} = 4.94 \text{ cm}^{-1}$ (2.47 cm^{-1}) obtained by Kim and co-workers agree with the values derived in this study [$A^+\zeta_{\text{ev}} = 4.90 \text{ cm}^{-1}$ (2.46 cm^{-1})] for CH_3I^+ (CD_3I^+). However, it appears that the values they used for A^+ were not derived from the

FIG. 3. High-resolution PFI-ZEKE photoelectron spectra of selected regions of the $\tilde{X}^+ 2E_{3/2} \leftarrow \tilde{X} 1A_1$ transition of CH_3I . (a) Main rotational band consisting of several overlapping $\Delta P = +3/2$ sub-bands. (b) Rotational sub-band with $|J, K = 0\rangle \rightarrow |J^+, P^+ = -3/2\rangle$. The experimental spectra [top panels in (a) and (b)] are compared with calculated stick spectra (bottom panels) and spectra obtained by convolution of the stick spectra with a Gaussian line profile with 0.15 cm^{-1} bandwidth in (a) and 0.25 cm^{-1} bandwidth in (b) (middle panels). In the bottom panel of (b) the lines are labeled by their branch index and the value of the ground-state rotational angular momentum quantum number J .

positions of the satellite bands of their MATI spectrum but from their earlier analysis of the $\tilde{A}^+ \leftarrow \tilde{X}^+$ transition.²⁴ In Ref. 24, the quantity $\Delta A^+ = A_X^+ - A_A^+ = 0.205(8) \text{ cm}^{-1}$ could indeed be derived with high accuracy, and values of $A_X^+ = A^+ = 5.200(8) \text{ cm}^{-1}$ and $A_A^+ = 4.995(8) \text{ cm}^{-1}$ were reported. Careful recalculation of the experimental spectrum of the $\tilde{A}^+ \leftarrow \tilde{X}^+$ transition presented in Fig. 2

of Ref. 24 leads us to the conclusion that only the quantity ΔA^+ can be extracted from this spectrum, and not A_X^+ , which seems to indicate that the value of 5.200 cm^{-1} used for A_X^+ has been taken from another source in Ref. 24. We, therefore, suspect that our value of A_X^+ is more reliable, and also that the A_A^+ value (4.995 cm^{-1}) reported in Ref. 24 might have to be reduced to $4.815(10) \text{ cm}^{-1}$.

TABLE II. Molecular parameters describing the structure and dynamics of the $2E_{3/2}$ vibronic ground state of CH_3I^+ and comparison to previous studies. The interval $\Delta E_{SO} = a\zeta_e d$ between the origins of the $2E_{1/2}$ and $2E_{3/2}$ states is -5053 cm^{-1} (Ref. 16).

	This work	Refs. 20 and 26	Ref. 18	Ref. 15	Ref. 16
E_I	$76931.35(20) \text{ cm}^{-1}$	$76934(5) \text{ cm}^{-1}$	$76930.7(5) \text{ cm}^{-1}$	$76934(5) \text{ cm}^{-1}$	$76932(4) \text{ cm}^{-1}$
A^+	$5.02(1) \text{ cm}^{-1}$	$5.2000(8) \text{ cm}^{-1}$			
B^+	$0.251(1) \text{ cm}^{-1}$	$0.25300(14) \text{ cm}^{-1}$			
ζ_{ev}	$0.9755(5)$	$[\zeta_e = 0.950(3)]$

FIG. 4. High-resolution PFI-ZEKE photoelectron spectra of selected regions of the $\tilde{X}^+ 2E_{3/2} \leftarrow \tilde{X} 1A_1$ transition of CD_3I . (a) Main rotational band consisting of several overlapping $\Delta P = +3/2$ sub-bands. (b) Rotational sub-bands with $|J, K = 0\rangle \rightarrow |J^+, P^+ = -3/2\rangle$ and $|J, K = -1\rangle \rightarrow |J^+, P^+ = -5/2\rangle$. The experimental spectra [top panels in (a) and (b)] are compared with calculated stick spectra (bottom panels) and spectra obtained by convolution of the stick spectra with a Gaussian line profile with 0.15 cm^{-1} bandwidth (middle panels). In the bottom panel of (b) the lines are labeled by their branch index and the value of the ground-state rotational angular momentum quantum number J . The discontinuity in the spectrum marked by an asterisk was caused by a mode hop of the ring laser.

V. DISCUSSION OF SELECTION RULES AND LINE INTENSITIES

A. Photoionization selection rules

The general rovibronic photoionization selection rules derived in Ref. 54

$$\begin{aligned} \Gamma_{\text{rve}} \otimes \Gamma_{\text{rves}}^+ &\supset \Gamma^* \quad \ell \text{ even,} \\ \Gamma_{\text{rve}} \otimes \Gamma_{\text{rves}}^+ &\supset \Gamma^{(s)} \quad \ell \text{ odd,} \end{aligned} \quad (19)$$

when applied to the $\tilde{X}^+ 2E_{3/2} \leftarrow \tilde{X} 1A_1$ photoionizing transition of CH_3I using the spin double group $C_{3v}^-(M)$ for which $\Gamma^* = A_2$ and $\Gamma^{(s)} = A_1$, lead to the set of allowed transitions summarized in Table IV. The same selection rules apply for even- ℓ and odd- ℓ photoelectron partial waves because $A_1 \otimes E = A_2 \otimes E = E$ and $E \otimes E = A_1 \oplus A_2 \oplus E$. These symmetry selection rules hardly impose any restrictions on the photoionizing transitions, nor do they enable one to classify transitions into groups associated with even- ℓ and odd- ℓ photoelectron partial waves.

A more restrictive set of photoionization selection rules can be obtained in the realm of the orbital ionization model described in Refs. 55 and 56. The degenerate (e) orbital of CX_3I ($X = H, D$) from which the electron is ejected can adequately be described as (p_x, p_y) atomic orbitals centered on the I atom. These orbitals have a nodal plane containing the molecular z axis and, therefore, a value of $\lambda = \pm 1$, where λ is the quantum number associated with the projection of the molecular-orbital angular momentum onto the

TABLE III. Molecular parameters describing the structure and dynamics of the $2E_{3/2}$ vibronic ground state of CD_3I^+ and comparison to previous studies. The interval $\Delta E_{SO} = a\zeta_e d$ between the origins of the $2E_{1/2}$ and $2E_{3/2}$ states is -5038 cm^{-1} (Ref. 15).

	This work	Refs. 20 and 26	Ref. 15
E_1	$76957.40(20) \text{ cm}^{-1}$	$76957(5) \text{ cm}^{-1}$	$76958(5) \text{ cm}^{-1}$
A^+	$2.53(1) \text{ cm}^{-1}$	$2.6015(8) \text{ cm}^{-1}$	
B^+	$0.205(1) \text{ cm}^{-1}$	$0.20300(14) \text{ cm}^{-1}$	
ζ_{ev}	$0.9730(5)$	$[\zeta_e = 0.950(3)]$	

molecular z axis. Removing an electron from the (e) orbital, therefore, generates an “electron hole” with $\lambda = \pm 1$, which translates into a propensity rule $\Delta K = K^+ - K = \pm 1$ for allowed rovibronic transitions. Because the center of mass of the molecule does not exactly correspond to the center of mass of the iodine atom, a single-center expansion of the (e) valence molecular orbital includes terms with $\ell_{\pm\lambda} = p_{\pm 1}, d_{\pm 1}, \dots, \ell_{\pm 1}^{\max}$, leading to a restriction in the number of observable rotational branches $\Delta J = J^+ - J$ given by $\Delta J_{\max} = \ell_{\max}^+ + 3/2, \dots, -\ell_{\max}^- - 3/2$. In the case of CH_3I^+ and CD_3I^+ , a single-center expansion with terms up to $\ell^{\max} = 2$ only (i.e., $|\Delta J_{\max}| = 7/2$) was found to be sufficient to reproduce the observed spectra (see Table I).

The orbital ionization model, as applied so far in polyatomic molecules,⁵⁶ has been restricted to transitions between neutral and ionic states both described by Hund’s-case-(b)-type angular-momentum coupling and has two main deficiencies in the present case. First, it disregards effects resulting from the spin–orbit coupling and does not, therefore, account for the projection Σ^+ of the electron spin in the $\tilde{X}^{+2}\text{E}$ cation. Second, it neglects configuration interactions and vibronic interactions, which is problematic for methyl iodide because the cation is subject to a Jahn–Teller effect. The first deficiency can be partially overcome by assuming that the orbital hole created upon photoionization has a total projection quantum number $\omega = \lambda + \sigma$ that equals the $\Omega = \Lambda + \Sigma$ value of the spin–orbit component of the cation produced by photoionization, i.e., $|\Omega| = 3/2$ and $1/2$ for $^2\text{E}_{3/2}$ and $^2\text{E}_{1/2}$, respectively [note that Ω is not the same quantity as $\Omega' = \Lambda - \ell_v + \Sigma$ defined in Eq. (7)]. This assumption leads to the selection rule $\Delta P = P^+ - K = \omega = \Omega$ instead of the selection rule $\Delta K = \pm 1$ derived above. The strong spin–orbit coupling in the ^2E state of the cation, therefore, makes it desirable to derive photoionization selection rules involving the quantum number $P = K + \Sigma$ rather than the quantum number K .

P is strictly a good quantum number of the cation only in the limit where the contribution from the spin–uncoupling term in Eq. (10) is small compared to $a\zeta_e d$. To avoid using P , Kim and co-workers^{20,25,26} chose to assign the rotational sub-bands observed in their MATI spectrum in terms of the value of ΔK , effectively disregarding the electron spin projection along the z axis, and derived the empirical selection rule $\Delta K = \pm 1$ and ± 2 from their spectrum. However, as pointed out in Refs. 20 and 26, and discussed in the Introduction, this selection rule predicts more rotational sub-bands than observed in the photoelectron spectra without providing a reason for the nonobservation of certain sub-bands.

TABLE IV. Allowed rovibronic photoionizing transitions for $\Gamma_{\text{ev}}^+ = \text{E} \leftarrow \Gamma_{\text{ev}} = \text{A}_1$ in the spin double group $\text{C}_{3v}^+(\text{M})$. The selection rules are the same for even- ℓ and odd- ℓ photoelectron partial waves.

$\Gamma_r = \Gamma_{\text{rve}}$	Γ_{ves}^+	Γ_r^+	Γ_{rves}^+
A_1/A_2	$\rightarrow \text{E}_{3/2} :$	$\text{E}_{3/2}$	$\text{A}_1 \oplus \text{A}_2$
	$\rightarrow \text{E}_{1/2} :$	$\text{E}_{1/2}$	$\text{A}_1 \oplus \text{A}_2 \oplus \text{E}$
E	$\rightarrow \text{E}_{3/2} :$	$\text{E}_{1/2}$	E
	$\rightarrow \text{E}_{1/2} :$	$\text{E}_{3/2}$	E
		$\text{E}_{1/2}$	$\text{A}_1 \oplus \text{A}_2 \oplus \text{E}$

Moreover, $\Delta K = \pm 2$ transitions are not compatible with the prediction $\Delta K = \pm 1$ of the orbital ionization model.

P is a good quantum number in the present case because the spin–uncoupling term is smaller than $a\zeta_e d$ [see Eq. (18)]. As shown in Sec. IV, the intense transitions observed in the PFI-ZEKE photoelectron spectrum of CH_3I and CD_3I conform to the selection rule $\Delta P = \Omega = +3/2$, but $\Delta P = -3/2$ transitions, though much weaker, are also observable and responsible for the satellite bands. The latter set of transitions cannot be explained by the simple argument presented above and requires additional considerations.

B. The orbital ionization model and its extension

In order to estimate the rotational line intensities of the spectrum of the $\tilde{X}^{+2}\text{E} \leftarrow \tilde{X}^1\text{A}_1$ ionizing transition in CH_3I and CD_3I , an orbital ionization model for transitions from a pure Hund’s-case-(b)-coupled neutral molecule to a Hund’s-case-(a)-coupled cation is needed. Buckingham *et al.*⁵⁵ have derived such a model for diatomic molecules by making the orbital approximation discussed in Sec. V A. Within this approximation, the total photoionization cross section is given as^{55,57}

$$\sigma_{\text{tot}} = \frac{8\pi^3 e^2 v q_v^2 k_s^2}{3c} \sum_{\ell=|\lambda|}^{\infty} \frac{1}{2\ell+1} Q(\ell) C_{\ell}^2 x_{\ell}, \quad (20)$$

where q_v^2 and k_s^2 stand for a Franck–Condon and a spin factor, respectively, and $Q(\ell)$ represents a geometric factor resulting from the angular-momentum coupling. The coefficients C_{ℓ} of the single-center expansion of the molecular orbital and the factor

$$x_{\ell} = \left[\ell \left| F_{n\ell}^{E,\ell-1} \right|^2 + (\ell+1) \left| F_{n\ell}^{E,\ell+1} \right|^2 \right], \quad (21)$$

which is a sum of two radial transition integrals, depend on the molecular orbital from which ionization occurs. The products $C_{\ell}^2 x_{\ell}$ are in general adjusted to match the experimental spectra (see Ref. 56).

In diatomic molecules, when ionization connects a Hund’s-case-(b)-coupled neutral state and a Hund’s-case-(a)-coupled ionic state, the geometric factor $Q(\ell)$ has the form⁵⁵

$$Q(\ell) = \frac{2J^+ + 1}{2S^+ + 1} \sum_{\chi=\ell-1/2}^{\ell+1/2} (2\chi + 1) \times \left(\begin{matrix} \ell & S^+ & \chi \\ \Delta\Lambda & \Sigma^+ & (\Lambda - \Omega^+) \end{matrix} \right)^2 \left(\begin{matrix} J^+ & \chi & N \\ -\Omega^+ & (\Omega - \Lambda) & \Lambda \end{matrix} \right)^2. \quad (22)$$

We now present an extension of the orbital ionization model for photoionizing transitions of polyatomic molecules connecting a Hund’s-case-(b)-coupled neutral with a Hund’s-case-(a)-coupled cationic state. Unlike in diatomic molecules, the rotational angular momentum of polyatomic molecules can have a nonzero projection onto the molecular z axis, and additional couplings between the spin, electronic, vibrational, and rotational angular momenta must be considered. Therefore, the $Q(\ell)$ factor describing a Hund’s-case-(b)-to-(a)

ionizing transition of a symmetric-top molecule involves the projections K and P^+ of the total angular momenta $\tilde{N} = \tilde{J}$ of the neutral molecule and $\tilde{J}^+$ of the ion:

$$Q(\ell) = \frac{2J^+ + 1}{2S^+ + 1} \sum_{\chi=\ell-1/2}^{\ell+1/2} (2\chi + 1) \times \begin{pmatrix} \ell & S^+ & \chi \\ \lambda & \sigma & -\Delta P \end{pmatrix}^2 \begin{pmatrix} J^+ & \chi & N \\ -P^+ & \Delta P & K \end{pmatrix}^2, \quad (23)$$

where λ and σ , the quantum numbers for the projections on the molecular z axis of the molecular orbital and spin angular momenta, respectively, are signed quantum numbers.

Calculations (not shown) of the PFI-ZEKE photoelectron spectra of the $^2E_{3/2}$ origins of CH_3I^+ and CD_3I^+ were carried out using the effective Hamiltonian $\hat{H}_{\text{RSO}}$ of Eq. (10), and with Eqs. (20) and (23) to model the intensity distributions. Equation (23) implies that, for CH_3I^+ in the vibronic state $|j = +1/2, \ell_v = 0, \Lambda = +1, \Sigma = +1/2\rangle$, only transitions obeying the selection rule $\Delta P = P^+ - K = \omega = +3/2$ are allowed, because the spin-electronic angular momentum $\omega = \lambda + \sigma$ of the photoelectron, within the orbital ionization model, corresponds to $\Omega' = \Omega = \Lambda + \Sigma = +3/2$ in the cation. Consequently, the orbital ionization model accounts for the main band of the photoelectron spectrum, corresponding to $\sim 90\%$ of the total intensity, but not for the weak satellite bands, which correspond to $\Delta P = P^+ - K = -3/2$, as already anticipated from symmetry considerations in Sec. V A. The calculations presented in Fig. 2 have clearly demonstrated the vibronic origin of the satellite bands. Given that the orbital ionization model does not include any effect of vibronic mixing, it is not surprising that it fails to account for these satellite bands, which must be regarded as being one of the signatures of the Jahn–Teller effect in this system.

The dominant effect of the vibronic mixing induced by the Jahn–Teller effect and the spin–orbit interaction is the admixture of a weak component of $\Omega' = -3/2$ character to the wavefunction [see second term on the right-hand side of Eq. (5)] which results in weakly allowed transitions with $\Delta P = \Omega' = -3/2$. This inclusion of this dominant vibronic contribution, therefore, provides a straightforward explanation for the satellite bands.

Transitions with $\Delta P = \pm 1/2$, however, remain forbidden in the presence of vibronic mixing and such transitions correspond to the nonobserved ΔK rotational sub-bands in Fig. 1. The inclusion of vibronic mixing in the spin double group, therefore, does not only account for the observation of the satellite bands with $\Delta P = -3/2$ that are forbidden within the orbital ionization model [Eq. (23)], but it also explains why some ΔK transitions allowed by the rovibronic selection rules in the $\text{C}_{3v}(\text{M})$ group are not observable. The same reasoning, when applied to the upper $E_{1/2}$ spin–orbit component [see Eq. (6)], leads to the selection rule $\Delta P = +1/2, -5/2$. In future, it will be interesting to also carry out a high-resolution photoelectron spectroscopic study of the $^2E_{1/2}$ state to verify this prediction.

VI. CONCLUSIONS

PFI-ZEKE photoelectron spectra of the lower spin–orbit component of the vibronic ground state of CH_3I^+ and CD_3I^+ have been recorded at a resolution sufficiently high to observe the rotational structure. This structure, which is complicated by the presence of satellite bands, could be reproduced with spectroscopic accuracy using an effective rovibronic Hamiltonian and a complete set of rovibronic photoionization selection rules. The analysis of the photoelectron spectra was carried out in the $\text{C}_{3v}^2(\text{M})$ spin double group, which correctly incorporates the strong Hund's-case-(a)-coupling character of the cations. Rovibronic photoionization selection rules and spectroscopic parameters determining the structure and dynamics in the CX_3I^+ , $\text{X} = \text{H}, \text{D}$, cations were derived. They quantify the joint effects of the Jahn–Teller effect and spin–orbit interaction in the limit where the spin–orbit interaction is dominant, and led to an understanding of the processes involved in photoionizing transitions connecting neutral and ionic states described by Hund's-case-(b)-type and Hund's-case-(a)-type angular momentum coupling, respectively.

The range of values the parameters a , d , and ζ_e can take in the $\tilde{X}^+{}^2E$ ground state of CH_3I^+ and CD_3I^+ is severely restricted by Eqs. (12) and (4) if one considers the values of ζ_{ev} determined here [$\zeta_{\text{ev}} = 0.9755(5)$ and $0.9730(5)$ for CH_3I^+ and CD_3I^+ , respectively] and the values of $\Delta E_{\text{SO}} = a\zeta_e d$ measured in Refs. 15 and 16 ($\Delta E_{\text{SO}} = -5053$ and -5038 cm^{-1} for CH_3I^+ and CD_3I^+ , respectively). The spin–orbit coupling constant of both isotopomers must have a value within the interval $[-5310 \text{ cm}^{-1} < a < -5180 \text{ cm}^{-1}]$ which lies midway between the spin–orbit coupling constant $a = -5069 \text{ cm}^{-1}$ of I (Ref. 58) and the spin–orbit coupling constant $a = -5404 \text{ cm}^{-1}$ of the $\text{X}^+{}^2\Pi$ state of HI^+ .⁵⁹ The parameter d , which represents the reduction factor of the spin–orbit splitting by the Jahn–Teller effect, is constrained to the interval $[0.95 \leq d < 1]$ which implies a very weak Jahn–Teller effect. Finally, the parameter ζ_e is restricted to the range $[0.97 \leq \zeta_e \leq 1]$ which indicates that the electron hole is centered around the I atom.

Within the series of methyl halide cations, CH_3I^+ represents a limiting case where the spin–orbit interaction is by far the dominant interaction leading to two well-separated states of $^2E_{3/2}$ and $^2E_{1/2}$ symmetry. In this limit, the Jahn–Teller effect only manifests itself by perturbations of the rotational structure in the form of satellite-band structures. These satellite bands turned out to be the key to understanding the Jahn–Teller effect in CH_3I^+ and the photoionization dynamics and selection rules, not only in CH_3I , but also in CH_3Cl , as will be discussed in the next article of this series.³³ The analysis of the spectra of CH_3I^+ and CD_3I^+ with Eq. (10) indicates that the satellite bands should be labeled by the spin-rovibronic quantum number P^+ and are of spin-rovibronic origin. The satellite bands are, therefore, of a different physical origin than the more frequently encountered pseudorotational progressions which depend on the vibronic quantum number j , are of vibronic origin, and are observed in the presence of a strong linear Jahn–Teller effect.^{1,60} The full resolution of the rotational structure achieved in the present study, therefore, provided new insights into the interplay of the Jahn–Teller

and spin-orbit interactions by revealing structures characteristic of Hund's-case-(a)-coupled systems with unprecedented detail.

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