Calculation of the vibronic structure of the photodetachment spectra of CCCl^- and CCBr^-

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The vibronic structure of the closely spaced and strongly coupled $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states in the photodetachment spectra of CCCl^- and CCBr^- has been calculated by considering Σ - Π vibronic coupling together with spin-orbit coupling. The stretching modes are treated within the so-called linear-vibronic-coupling model. The vibronic and spin-orbit parameters have been determined by accurate *ab initio* electronic-structure calculations. While the nonrelativistic vibronic-coupling parameters are of approximately equal strength in CCCl and CCBr , the vibronic-coupling parameters of spin-orbit origin are found to be larger in the latter. The calculated photodetachment spectra of both systems are shown to exhibit a complicated vibronic structure due to strong Σ - Π vibronic coupling. The spectral envelopes of the calculated photodetachment spectra exhibit a double-hump reminiscent of strongly coupled $E \times e$ Jahn-Teller systems. © 2006 American Institute of Physics. [DOI: 10.1063/1.2363193]

I. INTRODUCTION

Pure as well as heteroatom-doped carbon clusters have received much attention in recent years because of their astrochemical importance.^{1–6} Beyond their possible presence in interstellar and circumstellar spaces, small clusters consisting of two carbon centers and a first- or second-row element possess an interesting spectroscopic feature, i.e., the ground and first excited electronic states in these quasi-linear systems are very closely spaced. These close-lying electronic states show strong vibronic coupling (VC) which leads to the breakdown of the Born-Oppenheimer approximation. The most extensively studied system in this regard is CCH. The radical is known to possess a rather low-energy conical intersection of the potential-energy (PE) surfaces corresponding to the $^2\Sigma$ and $^2\Pi$ states. Several experimental and theoretical studies have been devoted to the understanding of the complicated spectroscopy of the $\tilde{A}^2\Pi$ - $\tilde{X}^2\Sigma^+$ system of this radical.^{7–19}

Halogen derivatives of this radical have also received some attention, with the aim to understand the effect of the electronegative atom on the geometry and the spectroscopy of the radical. While there have been limited studies on CCF (Refs. 20–23) and no attention has been paid to CCB and CCI, there exists a considerable amount of theoretical research on the electronic structure of CCl.^{21,24–30} Early

ab initio calculations of this radical by Largo *et al.*²¹ concluded the radical to be linear, with some ambiguities concerning the nature of the ground electronic state. While Hartree-Fock calculations with a small basis set predicted a $^2\Sigma$ ground state, calculations with improved basis sets and inclusion of electron correlation effects favored a $^2\Pi$ ground state.²¹ The energy separation between the two states was found to be less than 900 cm^{-1} .²⁴ A decade later the same authors suggested a nonlinear structure for the radical with a $^2A'$ ground state on the basis of density functional theory (DFT) calculations.²⁶ There has been no experimental information on the radical until recently, when Sumiyoshi *et al.* reported a detailed characterization of the CCl radical in the $\tilde{X}^2A'$ state by Fourier-transform microwave spectroscopy.³¹ Their experiment and corroborating *ab initio* studies lead to the conclusion that the ground state of the nonlinear radical has $^2\Sigma^+$ symmetry in the limit of linearity.³¹ They found the first excited electronic state to be only 200 cm^{-1} above the ground state, in contrast to the CCH radical, where this separation is about 3700 cm^{-1} .^{18,19} They have also recognized a $^2\Sigma^+$ - $^2\Pi$ conical intersection which is only 1200 cm^{-1} higher in energy than the minimum.³¹ This experimental study inspired Tarroni and Carter to perform a calculation of the infrared absorption spectrum of the radical.²⁹ These authors were the first to calculate the spin-orbit (SO) splitting of the $^2\Pi$ electronic state.

Other than CCX systems, the only well-studied quasilinear molecule in which the ground electronic state is involved

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in three-state VC is HCN^+ which is isoelectronic with CCH . Using the so-called linear VC model,³² Köppel *et al.* could explain the first band of the photoelectron spectrum³³ of HCN which is associated with closely spaced electronic states of Π and Σ symmetries.³⁴ Their assignments have been recently confirmed by high-resolution experiments³⁵ and high-level *ab initio* calculations.³⁶

Very recently, we have analyzed the VC of $^2\Pi$ and $^2\Sigma$ electronic states of quasi-linear molecules with the inclusion of SO coupling by employing the microscopic (Breit-Pauli) SO-coupling operator in the single-electron approximation.³⁷ We have derived a 6×6 Hamiltonian matrix in a diabatic spin-electronic basis, considering only the degenerate bending mode. It has been shown that there exist several novel Σ - Π VC terms of SO origin, which are absent when the usual phenomenological form of the SO coupling operator is used instead of its microscopic form, see Ref. 37. It has been demonstrated that the interplay of strong Σ - Π VC and strong SO splitting of the Π state can result in unexpectedly complex vibronic spectra. In the present work, we have combined the previous analysis for the bending mode with the treatment of the stretching modes within the so-called linear VC model^{32,38} to calculate the vibronic structure of the $^2\Sigma$ - $^2\Pi$ photodetachment spectra of the CCl^- and CCBr^- anions. We have determined the VC parameters from accurate *ab initio* calculations which are then used in the earlier developed Σ - Π SO-VC model³⁷ to calculate the vibronic struc-

ture of the $^2\Pi$ - $^2\Sigma$ photodetachment spectra of CCl^- and CCBr^- .

II. VIBRONIC HAMILTONIAN

We consider a single unpaired electron in a quasilinear molecule where a degenerate $^2\Pi$ state and a nondegenerate $^2\Sigma$ state are closely spaced. The degenerate bending vibrational mode of the linear molecule couples the two components of the degenerate $^2\Pi$ state in second order [Renner-Teller (RT) coupling] as well as the $^2\Sigma$ state with the $^2\Pi$ state in first order (Σ - Π coupling). The coupling of the orbital motion of the unpaired electron with its intrinsic spin converts this three-state problem to a system where six spin-electronic states are coupled via the degenerate bending mode. By using the Breit-Pauli SO operator, employing a diabatic spin-electronic basis and a Taylor series expansion of the diabatic PE surfaces as functions of the degenerate bending coordinate, the vibronic Hamiltonian corresponding to this system has been derived in Ref. 37. The SO coupling gives rise to several new VC terms which have not been considered in linear molecules, so far. While the bending mode couples the spin-electronic states, the totally symmetric stretching modes modulate the relative separation of the $^2\Sigma$ and $^2\Pi$ states as well as the SO splitting of the $^2\Pi$ state. Including the stretching modes in the so-called linear-vibrational-coupling approximation,³² the vibronic Hamiltonian is written as ($\hbar=1$)

$$\mathcal{H} = \mathcal{H}_b + \mathcal{H}_t, \quad (1)$$

$$\mathcal{H}_b = -\frac{\omega_2}{2} \left(\frac{1}{\rho} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} - \rho^2 \right) 1 + \begin{pmatrix} E_{\Pi,3/2} & \lambda \rho e^{i\phi} & c \rho^2 e^{2i\phi} & d \rho e^{i\phi} & h \rho^2 e^{2i\phi} & 0 \\ \lambda \rho e^{-i\phi} & E_{\Sigma,1,2} & \lambda \rho e^{i\phi} & g & 0 & -h \rho^2 e^{2i\phi} \\ c \rho^2 e^{-2i\phi} & \lambda \rho e^{-i\phi} & E_{\Pi,1/2} & 0 & -g & -d \rho e^{i\phi} \\ d \rho e^{-i\phi} & g & 0 & E_{\Pi,1/2} & \lambda \rho e^{i\phi} & c \rho^2 e^{2i\phi} \\ h \rho^2 e^{-2i\phi} & 0 & -g & \lambda \rho e^{-i\phi} & E_{\Sigma,1/2} & \lambda \rho e^{i\phi} \\ 0 & -h \rho^2 e^{-2i\phi} & -d \rho e^{-i\phi} & c \rho^2 e^{-2i\phi} & \lambda \rho e^{-i\phi} & E_{\Pi,3/2} \end{pmatrix}, \quad (2)$$

$$\mathcal{H}_t = \sum_{i=1,3} -\frac{\omega_i}{2} \left(\frac{\partial^2}{\partial Q_i^2} - Q_i^2 \right) + \sum_{i=1,3} \begin{pmatrix} \kappa_i^\Pi & & & & & \\ & \kappa_i^\Sigma & & & & \\ & & \kappa_i^\Pi & & & \\ & & & \kappa_i^\Pi & & \\ & & & & \kappa_i^\Sigma & \\ & & & & & \kappa_i^\Pi \end{pmatrix} Q_i. \quad (3)$$

Here $\mathcal{H}_b$ represents the vibronic Hamiltonian corresponding to the degenerate bending mode. ω_2 is the harmonic bending frequency, and ρ and ϕ are the radial and angular components of the dimensionless degenerate bending mode in polar representation, respectively. 1 is the 6

$\times 6$ unit matrix and $E_{\Pi,3/2}$, $E_{\Pi,1/2}$, and $E_{\Sigma,1/2}$ are the electronic energies at the reference geometry ($\rho=0$). To simplify the notation, we introduce the Σ - Π energy gap Δ and the SO splitting ζ as follows:

$$\Delta = E_{\Pi} - E_{\Sigma}, \quad (4)$$

$$\zeta = E_{\Pi,3/2} - E_{\Pi,1/2}. \quad (5)$$

Here E_{Π} and E_{Σ} are the electrostatic energies at the reference geometry, while $E_{\Pi,1/2}$ and $E_{\Pi,3/2}$ are the reference energies with inclusion of SO coupling. c is the well-known nonrelativistic quadratic RT coupling constant,^{39–42} λ is the linear Σ - Π coupling constant,⁴³ while g and h are purely relativistic Σ - Π coupling constants of zeroth and second order in the bending coordinate, respectively.³⁷ The parameter d is the relativistic linear RT coupling constant introduced in Ref. 44.

The zeros appearing along the cross diagonal are a consequence of the time-reversal symmetry. The two 3×3 diagonal blocks of the vibronic Hamiltonian (2) have the same form as the nonrelativistic Σ - Π Hamiltonian ($\zeta=0$).⁴³ The off-diagonal 3×3 blocks of the vibronic Hamiltonian (2) are, necessarily, of purely relativistic origin. $\mathcal{H}_t$ is the Hamiltonian of the two stretching modes with harmonic frequencies ω_1 and ω_3 and dimensionless normal coordinates Q_1 and Q_3 , respectively. The κ_i 's for the $^2\Sigma$ and $^2\Pi$ states are the linear electron-vibrational coupling constants^{32,38} which are given by the first derivatives of the PE terms $V(Q)$ with respect to dimensionless normal coordinates Q_i , i.e.,

$$\kappa_i = \left(\frac{\partial V(Q)}{\partial Q_i} \right)_0, \quad i = 1, 3. \quad (6)$$

$$\begin{pmatrix} 0 & 0 & i\zeta/2 & 0 & -\frac{g - h\rho^2 e^{2i\phi}}{\sqrt{2}} & id\rho e^{i\phi} \\ 0 & 0 & 0 & \frac{g - h\rho^2 e^{2i\phi}}{\sqrt{2}} & 0 & i\frac{g + h\rho^2 e^{2i\phi}}{\sqrt{2}} \\ -i\zeta/2 & 0 & 0 & -id\rho e^{i\phi} & -i\frac{g + h\rho^2 e^{2i\phi}}{\sqrt{2}} & 0 \\ 0 & \frac{g - h\rho^2 e^{-2i\phi}}{\sqrt{2}} & id\rho e^{-i\phi} & 0 & 0 & -i\zeta/2 \\ -\frac{g - h\rho^2 e^{-2i\phi}}{\sqrt{2}} & 0 & i\frac{g + h\rho^2 e^{-2i\phi}}{\sqrt{2}} & 0 & 0 & 0 \\ -id\rho e^{-i\phi} & -i\frac{g + h\rho^2 e^{-2i\phi}}{\sqrt{2}} & 0 & i\zeta/2 & 0 & 0 \end{pmatrix}. \quad (7)$$

The matrix of Eq. (7) represents the matrix elements of the Breit-Pauli SO operator with nonrelativistic *adiabatic* electronic wave functions. The SO splitting ζ and the zeroth-order relativistic Σ - Π coupling term g are obtained at the linear geometry. The parameters d and h can be extracted from the slope and the curvature of the corresponding SO matrix elements as a function of the bending coordinate, respectively.

CCCl^- and CCBr^- are closed-shell linear systems in their ground electronic state $\tilde{X}^1\Sigma$ with the following valence-shell electronic configuration: $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi^4 4\sigma^2$. While the 4σ molecular orbital is a nonbonding orbital

Other than in the RT case,⁴⁵ where the discussion is restricted to an isolated degenerate electronic state, the stretching and bending modes of the linear molecule cannot be decoupled in the case of Σ - Π coupling. Note that in Eq. (3) we have neglected the gradients of the SO splitting ζ with respect to the stretching modes, which are expected to be small compared to the nonrelativistic energy gradients.

III. *AB INITIO* CALCULATION OF PARAMETERS

A. Computational methods

For molecules with not too heavy atoms, it is a good approximation to compute the VC terms of SO origin from the matrix elements of the Breit-Pauli SO operator with nonrelativistic basis functions. The electronic basis states obtained by the *ab initio* electronic-structure calculations are the nonrelativistic *adiabatic* states, which correspond to the diagonalization of the nonrelativistic fixed-nuclei electronic Hamiltonian $\mathcal{H}_b^{\text{nr}}$. Using the unitary matrix that diagonalizes $\mathcal{H}_b^{\text{nr}}$ and performing a corresponding similarity transformation of the relativistic part of the vibronic Hamiltonian (2), we arrive at the following transformed form of the SO part of the Hamiltonian:

localized on the terminal C atom, the 2π molecular orbital is essentially a CC π bonding orbital. Removal of an electron from the 4σ and 2π molecular orbital gives rise to the ground and first excited electronic states of the corresponding radical, i.e., the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states, respectively.

We have employed the augmented correlation-consistent polarized valence triple-zeta (aug-cc-pVTZ) basis set of Dunning^{46,47} for the C and Cl atoms. For Br, we have used a relativistic-effective-core potential (RECP), where the core orbitals (i.e., $1s$ - $3d$, with 28 electrons) are described by a semilocal energy-adjusted pseudopotential of the energy-consistent variety.⁴⁸ The valence orbitals of Br are described

by optimized contracted *s*-, *p*-, *d*-, and *f*-type functions of augmented triple-zeta quality.⁴⁸ Using this basis set, we have optimized the geometry of the anions in their ground states and have calculated the harmonic frequencies with DFT, using Becke's three-parameter hybrid functional with the LYP correlation functional (B3LYP).⁴⁹ The DFT calculations have been performed using the GAUSSIAN package.⁵⁰ In addition to the DFT calculations, we also have performed coupled cluster (CC) calculations including single, double, and perturbative triple excitations⁵¹ [CCSD(T)] to determine the optimized geometries of the anions. The CC calculations have been performed with the MOLPRO program suite.⁵²

The averaged bending frequency ω_2 , the nonrelativistic quadratic RT coupling parameter *c*, and the nonrelativistic Σ - Π coupling term λ have been obtained by performing a nonlinear least-squares fit of the PE curves of the two components of the $\tilde{A}^2\Pi$ state and the $\tilde{X}^2\Sigma^+$ state as a function of the bending coordinates (ρ, ϕ). The two $\tilde{A}^2\Pi$ bending PE curves, which touch each other at the linear geometry, and that of the $\tilde{X}^2\Sigma^+$ state have been obtained by performing a state-averaged full-valence complete-active-space self-consistent-field (CASSCF) calculation at the ground-state reference geometry of the stretching modes.^{53,54} Here, all the inner valence electrons are kept frozen, resulting in the correlation of 15 electrons in 12 orbitals, i.e., a (15, 12) CASSCF calculation.

The matrix elements of the Breit-Pauli SO operator with nonrelativistic wave functions have been computed, yielding the SO splitting ζ , the linear-relativistic RT parameter *d* as well as the zeroth- and second-order relativistic parameters (*g* and *h*), as described above. The nonrelativistic wave functions have been obtained by performing a state-averaged (over the degenerate $\tilde{A}^2\Pi$ state and the nondegenerate $\tilde{X}^2\Sigma^+$ state) full-valence (15, 12) CASSCF calculation.^{53,54} In the case of CCB_r, the SO matrix elements have been determined by employing the SO-pseudooperator of Dolg⁵⁵ for the Br atom, adapted to the above cited scalar RECP. The MOLPRO software has been used for the SO calculations.^{52,56}

The linear VC constants of the stretching modes (κ_i) for the $\tilde{X}^2\Sigma^+$ and the $\tilde{A}^2\Pi$ states have been calculated according to the expression

$$\kappa_i = \sqrt{\frac{\hbar}{\omega_{ij=1,3}}} \sum L_{ij} \left(\frac{\partial V(Q)}{\partial R_j} \right)_0, \quad i = 1, 3. \quad (8)$$

Here, the R_j are the two bond distances. The *L* matrix is obtained by the simultaneous diagonalization of the *F* and *G* matrices.⁵⁷ The *G* matrix has been constructed from the molecular geometry parameters and atomic masses,⁵⁷ while the *F* matrix has been obtained from a force-field calculation using the DFT/B3LYP method. The gradients $\partial V / \partial R_j$ for the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states have been determined by a CCSD(T) calculation for the radicals. The vertical detachment energies of the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states of the corresponding radicals at the ground-state equilibrium geometry of the anions have been obtained from the difference of the CCSD(T) energies of these states and the $\tilde{X}^1\Sigma$ state of the corresponding anions, and is denoted by $\Delta\text{CCSD(T)}$. The difference between

TABLE I. Bond distances (in Å) and harmonic vibrational frequencies (in cm^{-1}) of the ground state of CCX^- .

Parameter	CCCl^-	CCBr^-
$R_0(\text{CC})$	1.2404 ^a	1.2419 ^a
	1.2566 ^b	1.2585 ^b
	1.2430 ^c	
$R_0(\text{CX})$	1.6975 ^a	1.8490 ^a
	1.7049 ^b	1.8526 ^b
	1.708 ^c	
ω_1	2006.8 ^a	1992.2 ^a
	1937.1 ^b	1918.2 ^b
ω_2	254.1 ^a	221.0 ^a
	226.0 ^b	203.1 ^b
ω_3	640.3 ^a	521.2 ^a
	633.3 ^b	512.7 ^b

^aDFT/B3LYP.

^bCCSD(T).

^cReference 26.

the energies of the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states provides the Σ - Π splitting Δ , see Eq. (4).

B. Results

1. CCCl^-

The CC and CCl bond distances in the ground electronic state of CCCl^- have been obtained as 1.2404 and 1.6975 Å from the DFT calculation, while the CCSD(T) method predicts a slightly longer bond length for both CC and CCl bonds, see Table I. The CC bond length of CCCl^- is longer than the bond length of the triple bond of acetylene. This suggests that the CC bond order in CCCl^- is less than three, which is expected due to the presence of an electronegative atom such as Cl which also contains electrons in its *p* orbitals.^{21,58} The calculated bond distances are in good agreement with the values obtained in Ref. 26, see Table I. The harmonic vibrational frequencies are obtained as 2006.8 cm^{-1} (CC stretch), 254.1 cm^{-1} (CCCl bend), and 640.3 cm^{-1} (CCl stretch) from the DFT/B3LYP calculation. The CCSD(T) method predicts smaller values of harmonic frequencies for all vibrational modes, see Table I. From the nonlinear least-squares fit of the *ab initio* PE curves of the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states along the bending coordinate obtained by a (15,12) CASSCF calculation, the averaged bending frequency, the quadratic RT parameter, and the linear Σ - Π coupling parameter are obtained as 377.8, 30.5, and 718.3 cm^{-1} , respectively. The overall quality of the fit, determined from the square root of the mean-squared deviation of the *ab initio* calculated energy from the adiabatic PE functions, is less than 1 cm^{-1} . Note the change in the averaged bending frequency of the $\tilde{X}^2\Sigma^+$ - $\tilde{A}^2\Pi$ states of CCl compared to the harmonic bending frequency of the $\tilde{X}^1\Sigma$ state of CCCl^- . This change is a consequence of the nonlinear ground-state equilibrium geometry of the CCl radical, which has been the subject of discussion in several articles.^{21,24,26,28,29,31,58} The large value of the nonrelativistic Σ - Π coupling term

TABLE II. Vibronic-coupling parameters (in cm^{-1}) of the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states of CCX . The numbers in parentheses are the values in units of ω_2 . See Eq. (2) for the definition of the coupling parameters.

Parameter	CCCl	CCBr
ω_2	377.8 ^a 354.0 ^b	361.7 ^a
c	30.5(0.08) ^a	30.0(0.08) ^a
λ	718.3(1.90) ^a	714.6(1.98) ^a
ζ	-85(0.23) ^c -101.2 ^d	-290.1(0.81) ^c
d	1.6(0.00) ^c	20.7(0.06) ^c
g	22.2(0.06) ^c	156.3(0.43) ^c
h	0.0(0.00) ^c	0.0(0.00) ^c

^aFrom the least-squares fitting of the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ state averaged CASSCF PE functions.

^bReference 31.

^cFrom the matrix elements of the SO operator with the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ state-averaged CASSCF basis functions.

^dReference 29.

(nearly twice the averaged bending frequency) implies a very strong vibronic interaction of the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states. The quadratic RT coupling term has a rather moderate value, i.e., one-tenth of the averaged bending frequency, see Table II.

The SO splitting of the $\tilde{A}^2\Pi$ state is calculated as -85 cm^{-1} . Tarroni and Carter have calculated the SO splitting as -101 cm^{-1} at the equilibrium geometry of the $^2\Pi$ state.²⁹ The negative value implies that the $^2\Pi_{3/2}$ component is lower in energy than the $^2\Pi_{1/2}$ component. The rather small value of the SO splitting is due to the fact that the $^2\Pi$ state is mostly a CC π orbital with small electron density on the Cl atom. The linear relativistic VC term d is small (1.6 cm^{-1}) and the SO splitting of the $^2\Pi$ state is considerably smaller than the averaged bending frequency. Therefore, no significant perturbations of the spectra by the linear relativistic coupling term $dpe^{\pm i\phi}$ are expected.^{45,59} The zeroth-order relativistic Σ - Π coupling term g is calculated as 22.2 cm^{-1} , which is nearly one-tenth of the averaged bending frequency. The quadratic relativistic Σ - Π coupling term h , on the other hand, is negligibly small.

The VC parameters of the stretching modes are given in Table III. The so-called Poisson parameters ($\kappa_i^2/2\omega_i^2$) are shown in parentheses. The vibrational couplings of the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states are relatively weak along the CC stretching mode. The CCl stretching mode, on the other hand, is more strongly coupled, especially in the $\tilde{A}^2\Pi$ state, see Table III. The adiabatic PE functions of the linear VC model are com-

TABLE III. The linear electron-vibrational coupling constants of the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states of CCX (in cm^{-1}) obtained from the CCSD(T)/AVTZ calculation. The numbers in parentheses are the so-called Poisson parameters ($\kappa_i^2/2\omega_i^2$).

	CCCl		CCBr	
	$\tilde{X}^2\Sigma^+$	$\tilde{A}^2\Pi$	$\tilde{X}^2\Sigma^+$	$\tilde{A}^2\Pi$
κ_1	1405.0(0.25)	-1461.5(0.26)	1370.5(0.24)	-1403.6(0.25)
κ_3	684.4(0.57)	926.1(1.05)	520.5(0.50)	741.6(1.02)

FIG. 1. Comparison of the adiabatic potential-energy functions of the linear vibronic-coupling model (solid lines) with *ab initio* CCSD(T) energies (crosses) for the stretching modes Q_1 and Q_3 of CCl .

pared with the *ab initio* CCSD(T) energies in Fig. 1, as a function of the Q_1 and Q_3 modes. The excellent agreement between the two suggests that the linear VC approximation is appropriate for the present problem.

The calculated vertical detachment energies of the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states of the CCCl radical are given in Table IV. While the $^2\Sigma$ state is found to be 3.56 eV above the ground state of the anion at the equilibrium geometry of the latter, the $^2\Pi$ state is found only about 156 cm^{-1} above the $^2\Sigma$ state. The latter result is in very good agreement with the most recent experimental determination, where the $\tilde{A}^2\Pi$ state is reported to be around 200 cm^{-1} above the $\tilde{X}^2\Sigma^+$ state.³¹

2. CCB r^-

The CC bond distance of CCBr^- is nearly the same as in CCCl^- . The CBr bond distance is calculated as $1.8490 \text{ \AA}$ with the B3LYP functional. As found for CCCl^- , the CCSD(T) method predicts longer bond distances, see Table I. The harmonic vibrational frequencies of CCBr^- , shown in Table I, are smaller than the corresponding values of CCCl^- , as a consequence of the larger mass of Br. The nonlinear least-squares fit of the state-averaged CASSCF PE curves of the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states yielded values for the averaged bending frequency (ω_2), the RT parameter (c), and the non-relativistic Σ - Π coupling parameter (λ) which are similar to

TABLE IV. Vertical detachment energy (VDE) and $\tilde{X}^2\Sigma^+ - \tilde{A}^2\Pi$ splitting (Δ) of CCX (in eV), obtained from CCSD(T)/AVTZ calculations. The numbers in parentheses are the value in cm^{-1} .

	C_2Cl		C_2Br	
	$\tilde{X}^2\Sigma^+$	$\tilde{A}^2\Pi$	$\tilde{X}^2\Sigma^+$	$\tilde{A}^2\Pi$
VDE	3.5599	3.5792	3.5860	3.6021
Δ	0.0193(155.6)		0.0162(130.6)	
	0.0248(200.0) ^a			
	0.0609(491.0) ^b			

^aReference 31.

^bReference 29.

FIG. 2. Comparison of the adiabatic potential-energy functions of the linear vibronic-coupling model (solid lines) with *ab initio* CCSD(T) energies (crosses) for the stretching modes Q_1 and Q_3 of CCB r .

those of CCCI $^-$. This is the consequence of the very limited contribution of the p orbitals of the halogen atom to the two highest occupied molecular orbitals of the anion. The large difference between the harmonic bending frequency of the anion and the averaged bending frequency of the radical suggests a nonlinear equilibrium geometry of the radical. The overall root-mean-square error of the fit is less than 1 cm^{-1} .

The SO splitting is calculated as -290 cm^{-1} , which is about 80% of the averaged bending frequency. The bending frequency and the SO splitting of the $^2\Pi$ state are thus nearly in resonance. The linear relativistic VC parameter d is small, less than one-tenth of the averaged bending frequency. On the other hand, we obtain a very large value for the zeroth-order relativistic Σ - Π coupling parameter (g) which is nearly half the averaged bending frequency, see Table II. The second-order relativistic Σ - Π coupling parameter h again has a negligible value. We have also performed a core-polarization potential (CPP) calculation⁴⁸ for Br to determine the SO matrix elements. The effect of the core polarization is found to be negligible.

The VC parameters of the stretching modes are shown in Table III with the so-called Poisson parameters ($\kappa_i^2/2\omega_i^2$) in parentheses. The Poisson parameters have similar values as for CCCI $^-$, i.e., the coupling of the CC stretching mode is weak and that of the CBr mode is strong, see Table III. The adiabatic PE curves of the linear VC model are in excellent agreement with the *ab initio* CCSD(T) energies along both the stretching modes, (see Fig. 2) thus suggesting the validity of the linear VC model.

The calculated vertical detachment energies of the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states of the radical with respect to the ground state of the anion are given in Table IV. They are similar to those of CCCI. The Σ - Π splitting is calculated as 131 cm^{-1} . To our knowledge, this is perhaps the smallest known vertical energy difference between the ground state and the first excited state of any linear triatomic system.

IV. CALCULATION OF SPECTRA

The vibronic Hamiltonian $\mathcal{H}_b$ of Eq. (2) commutes with the z projection of the electronic and vibrational angular momentum J_z given by

$$J_z = \frac{1}{i} \frac{\partial}{\partial \theta} + \sigma_z + \frac{1}{i} \frac{\partial}{\partial \phi}, \quad (9)$$

where θ is the electronic azimuthal angle and σ_z is the z projection of the spin angular momentum. Hence the half-integral eigenvalues (μ) of J_z are good quantum numbers. We assume the anion to be vibrationally cold, that is, we consider ionization from the vibrationless electronic ground state. In this case, μ can take the values $\pm 1/2$ and $\pm 3/2$. It therefore suffices to construct and diagonalize the vibronic Hamiltonian matrix for $\mu=1/2$ and $\mu=3/2$.

We represent $\mathcal{H}$ as a matrix in the direct-product basis of diabatic electronic states and the appropriate unperturbed harmonic oscillator eigenstates. For each vibrational mode, the basis is suitably truncated. A rough estimate of the maximum level of excitation for each mode can be obtained from the Poisson parameters of the corresponding mode. For a given value of μ , the highly sparse Hamiltonian matrix is first tridiagonalized by the Lanczos algorithm,^{60,61} followed by the diagonalization of the symmetric tridiagonal matrix. The eigenvalues represent the line positions. While $\mu=3/2$ levels gain intensity from the $^2\Pi_{3/2}$ state, $\mu=1/2$ levels gain intensity from both the $^2\Pi_{1/2}$ and $^2\Sigma_{1/2}$ states. Thus for $\mu=1/2$ two different Lanczos starting vectors are used, one for the $^2\Pi_{1/2}$ state and the other for the $^2\Sigma_{1/2}$ state. The relative intensities are obtained from the squared first components of the final Lanczos vectors.^{38,61} The calculated spectrum is finally convoluted with a normalized Lorentzian of finite width to account for rotational broadening and the finite resolution of experimental photodetachment spectra. Since we are concerned with relativistic VC, which sometimes has very small effects on the line positions and spectral intensities, we have chosen a rather small value (1 meV) for the Lorentzian width.

Since CCCI $^-$ and CCB r^- have similar Poisson parameters for all vibrational modes, the number of harmonic oscillator basis functions used for the calculation of the final spectra is the same. The appropriate values of the maximum vibrational quantum number of different modes are found as 25 (CCX bending), 14 (CX stretching), and 7 (CC stretching). Thus a Hamiltonian matrix of the dimension 14700 has been diagonalized by performing 1500 Lanczos iterations. The origin of the spectra is adjusted to the detachment energy of the $\tilde{X}^2\Sigma^+$ state.

V. DISCUSSION OF THE PHOTODETACHMENT SPECTRA

A. CCCI $^-$

The calculated vibronic structure of the photodetachment spectrum of CCCI $^-$ is shown in Fig. 3. In the upper panel, the pure bending spectrum is shown, i.e., the stretching modes are absent. The solid, dashed, and dotted lines represent vibronic levels which gain intensity from the $^2\Pi_{3/2}$, $^2\Pi_{1/2}$, and

FIG. 3. Calculated vibronic structure of the $\tilde{X}^2\Sigma^+ - \tilde{A}^2\Pi$ photodetachment spectrum of CCl . (a) Only the bending vibrational mode is considered. The solid, dashed, and dotted lines represent vibronic levels which gain intensity from the $^2\Pi_{3/2}$, $^2\Pi_{1/2}$, and $^2\Sigma_{1/2}$ states, respectively. (b) All vibrational modes are included.

$^2\Sigma_{1/2}$ states, respectively. Most of the peaks of $^2\Pi$ origin appear as closely spaced doublets. This reflects the small SO splitting and moderate RT coupling. The $\tilde{X}^2\Sigma^+$ ground state gives rise to the progression of dotted lines in Fig. 3(a). It is noteworthy that this progression exhibits a double-hump spectral envelope which is typical for strongly coupled Jahn-Teller systems.^{42,62–65} The pure bending spectrum is quite complicated with many quasidegenerate levels. The reason for the complicated structure is primarily the very small Σ - Π splitting and the strong nonrelativistic Σ - Π coupling.

Figure 3(b) shows the calculated photodetachment spectrum with all the three modes included. The spectrum is unusually complex with many peaks of small or medium intensity. Several closely spaced doublets, belonging to the $\tilde{A}^2\Pi$ state, can still be identified. It is very difficult to assign the individual peaks due to the strong vibronic mixing of most levels. The low-energy part of the spectrum is mainly due to bending excitations, while the high-energy levels involve excitations of the stretching modes. The overall envelope of the spectrum exhibits two broad humps. This shape of the spectrum might suggest the assignment of the two bands as the spectral structures of two separate electronic states. In reality, however, the two electronic states are closely spaced and the double-hump shape arises from the strong Σ - Π coupling of both nonrelativistic and relativistic origins.

B. CCBr^-

The calculated photodetachment spectrum of CCBr^- is shown in Fig. 4. The upper panel of the figure shows the pure bending spectrum. In Fig. 4(a) the solid, dashed, and dotted lines represent vibronic levels which gain intensity from the $^2\Pi_{3/2}$, $^2\Pi_{1/2}$, and $^2\Sigma_{1/2}$ states, respectively. The near degeneracy of the vibronic levels of the $^2\Sigma_{1/2}$ and the $^2\Pi_{3/2}$ states is the consequence of the accidental degeneracy of these two states. Similar to CCCl^- , the vibronic levels of the two SO

FIG. 4. Calculated vibronic structure of the $\tilde{X}^2\Sigma^+ - \tilde{A}^2\Pi$ photodetachment spectrum of CBr . (a) Only the bending vibrational mode is considered. The solid, dashed, and dotted lines represent vibronic levels which gain intensity from the $^2\Pi_{3/2}$, $^2\Pi_{1/2}$, and $^2\Sigma_{1/2}$ states, respectively. (b) All vibrational modes are included.

components of the $\tilde{A}^2\Pi$ state appear as doublets. The doublet splittings are larger owing to the larger SO splitting in CCBr . The $\tilde{X}^2\Sigma^+$ state gives rise to a double-hump spectral envelope, see Fig. 4(a).

Figure 4(b) shows the complete calculated photodetachment spectrum of CCBr^- . The lower energy part of the spectrum is again dominated by bending excitations, whereas the high-energy part contains many densely spaced peaks with medium and low intensities. The spectrum is more complicated than that of CCCl^- because of a strong relativistic zeroth-order Σ - Π vibronic coupling in CCBr . The overall shape of the spectrum again appears as a double hump.

VI. CONCLUSIONS

The vibronic structure of the coupled $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states in the photodetachment spectra of CCCl^- and CCBr^- has been calculated with the inclusion of nonrelativistic as well as relativistic RT and Σ - Π vibronic coupling. The stretching modes have been included in the linear VC approximation. The parameters of the model have been determined from accurate *ab initio* calculations.

The CCCl and CCBr radicals, like the CCH radical, exhibit closely spaced $^2\Sigma$ and $^2\Pi$ states with strong Σ - Π VC. The $^2\Sigma$ state has been found to be the ground state at the equilibrium geometry of the corresponding anion. The Σ - Π splittings are calculated as 156 and 131 cm^{-1} for CCCl and CCBr , respectively. The separation of the two states is strongly modulated by the stretching coordinates. While the nonrelativistic VC parameters are of approximately equal strength in both cases, the relativistic VC is stronger in CCBr than in CCCl .

The calculated photodetachment spectra of CCCl^- and CCBr^- have similar vibronic structure. While the low-energy part is dominated by peaks from bending excitations, the high-energy region exhibits a high density of vibronic levels

involving excitations of bending and stretching modes. The spectral envelopes exhibit a double-hump reminiscent of strongly coupled $E \times e$ Jahn-Teller systems. It is hoped that the theoretical predictions stimulate the recording of the $\tilde{X}^2\Sigma^+ - \tilde{A}^2\Pi$ photodetachment spectra of CCCl^- and CCBr^- .

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