Excited-state geometries and vibrational frequencies studied using the analytical energy gradients of the direct symmetry-adapted cluster–configuration interaction method. I. HAX-type molecules

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In this series of studies, we systematically apply the analytical energy gradients of the direct symmetry-adapted cluster–configuration interaction singles and doubles nonvariational method to calculate the equilibrium geometries and vibrational frequencies of excited and ionized states of molecules. The harmonic vibrational frequencies were calculated using the second derivatives numerically computed from the analytical first derivatives and the anharmonicity was evaluated from the three-dimensional potential energy surfaces around the local minima. In this paper, the method is applied to the low-lying valence singlet and triplet excited states of HAX-type molecules, HCF, HCCl, HSIF, HSiC, HNO, HPO, and their deuterium isotopomers. The vibrational level emission spectra of HSIF and DSIF and absorption spectra of HSiC and DSiC were also simulated within the Franck–Condon approximation and agree well with the experimental spectra. The results show that the present method is useful and reliable for calculating these quantities and spectra. The change in geometry in the excited states was qualitatively interpreted in the light of the electrostatic force theory. The effect of perturbation selection with the localized molecular orbitals on the geometrical parameters and harmonic vibrational frequencies is also discussed. © 2011 American Institute of Physics. [doi:10.1063/1.3617233]

I. INTRODUCTION

Electronic properties, geometric structures, and spectroscopic constants in molecular excited states are of interest because they are characteristics compared with those in the ground states. Recent developments in high-resolution spectroscopy have enabled us to obtain precise information on such quantities. Geometry relaxation and dissociation dynamics in the excited states can be elucidated by analyzing the fine structure arising from the vibrational spectra. Theoretical information is valuable for interpreting these high-resolution spectra and the physics behind them. Thus, the interplay between experiment and theory has become relevant in modern molecular spectroscopy.

Theoretical spectroscopy has been achieved using various electronic structure theories. Peyerimhoff and co-workers performed pioneering work using the multireference singles and doubles configuration interaction (MRSDCI) method.1 Nakatsuji has developed the symmetry-adapted cluster expansion (SAC)/symmetry-adapted cluster–configuration interaction (SAC–CI) (Refs. 2–4) method to study molecular excited states based on cluster expansion. Multireference cluster-expansion theories have also been developed for quasidegenerate systems.5 Various types of multireference-type perturbation theories, such as complete-active-space perturbation theory (CASPT2) (Ref. 6) and multireference second-order Møller–Plesset perturbation theory,7 have also been proposed and applied to molecular excited states. For theories aimed at theoretical spectroscopy, the development of analytical energy gradients is also a relevant issue because the derivatives of the potential energy surfaces (PESs) are key fundamental quantities to investigate the geometries, vibrations, and energy relaxation processes of the excited-state molecules.

The SAC/SAC–CI method has been established for investigating molecular excited states through numerous applications over a wide field of chemistry and physics. The method has been applied to molecular spectroscopy, biological chemistry, material science, and surface photochemistry.4,8 The analytical energy gradients of the SAC/SAC–CI method have also been formulated and implemented.9,10 The method has been applied to the calculation of equilibrium geometries and one-electron properties, such as dipole moments in various electronic states. It should be noted that the SAC–CI analytical energy gradient method is applicable to the higher excited states that cannot be accessed by ground-state theories such as quadratic configuration interaction singles and doubles (QCISD) (Ref. 11) and CCSD(T).12

The analytical energy gradients of the SAC/SAC–CI method have been applied to the geometry optimization
of molecules in excited, ionized, electron-attached, and high-spin states.\textsuperscript{5,10} Although this approach is useful for calculating force constants and vibrational frequencies, the method has not been utilized for this purpose. Behind this, there is one central issue: accurate calculation of the PESs and the energy derivatives is necessary to guarantee the reliability of the calculations of these quantities. In the SAC–CI method, we use the perturbation-selection approach,\textsuperscript{13} which is effective for large-scale calculations; however, this may involve the possibility of introducing an inaccuracy in calculating vibrational frequencies. Recently, a direct algorithm for the SAC/SAC–CI method has been developed,\textsuperscript{14} and the calculation of all the necessary product operators without any selection has become possible. This method is expected to be useful in calculating the vibrational frequencies.

Taking account of these issues in this series of studies, we systematically investigate the excited-state geometries and vibrational frequencies of the valence and core-excited/ionized states using the analytical energy gradients of the direct SAC/SAC–CI method at the singles and doubles (SD–R) level. We examine the various electronic states in singlet, doublet, and triplet spin multiplicities that can be calculated by the direct SAC–CI method and its analytical energy gradients. Therefore, we have selected electronic states that have been well studied by both experiments and theories. We have also calculated some higher electronic and vibrationally excited states that have not been examined so far.

The vibrational energy levels and the Franck–Condon (FC) factors between the different electronic states have also been extensively investigated based on accurate \textit{ab initio} PESs. For small systems, such as triatomic molecules, the grid method is a straightforward and powerful approach to calculating the vibrational energy levels and FC factors. Recently, postvibrational self-consistent field theories, such as vibrational configuration interaction (VCI),\textsuperscript{15} vibrational Möller–Plesset perturbation,\textsuperscript{16} and vibrational coupled-cluster\textsuperscript{17} methods have been developed for calculating the vibrational levels of polyatomic molecules. An efficient approach known as the scaled hypersphere search method\textsuperscript{18} has also been developed. In all of these methods, accurate calculation of the PESs is the most relevant issue.

The equilibrium geometries and spectroscopic constants of excited states of triatomic molecules have been extensively studied and much experimental data have been accumulated. Recently, accurate spectroscopic constants have been determined for HSiF (DSiF) (Refs. 19 and 20) and HSiCl (DSiCl) (Refs. 21 and 22) using high-resolution single vibronic level (SVL) emission spectroscopy and laser induced fluorescence (LIF) spectroscopy. Accurate theoretical calculations of the absorption and emission spectra were also performed for these molecules.\textsuperscript{23,24} The HCF,\textsuperscript{25} HCCI,\textsuperscript{26,27} and HAO (A = N, P) (Ref. 28) molecules that have isovalence electronic structures to HSIX (X = F, Cl) were also investigated by some experimental and theoretical studies. These molecules show characteristic geometry changes in the excited states and their spectroscopic constants have been intensively investigated for several electronic states and, therefore, the excited states of these molecules are good benchmarks for the present study.

Thus, in this work, we applied the direct SAC–CI method and its analytical energy gradients to the valence excited states of triatomic monohydrides, HCX (X = F, Cl), HSIX (X = F, Cl), and HAO (A = N, P), and their deuterium isomers to calculate the excited-state equilibrium geometries, vibrational frequencies, and adiabatic excitation energies. The harmonic vibrational frequencies have been numerically calculated using the analytical first derivatives and the anharmonicities have been evaluated using the three-dimensional (3D) PESs around the local minima. The vibrational level emission spectra of HSiF and DSiF and absorption spectra of HSICl and DSICl were also simulated within the FC approximation. The geometry change in the excited states is qualitatively interpreted based on the electrostatic force (ESF) theory.\textsuperscript{29} Perturbation selection with the localized molecular orbitals (LMOs) combined with the minimum-orbital deformation (MOD) method\textsuperscript{30} is also examined for calculating the excited-state equilibrium geometries and harmonic vibrational frequencies.

II. COMPUTATIONAL DETAILS

All of the geometry optimizations for the valence excited states were performed by the analytical energy gradients with the direct SAC–CI SD–R variational method. The vibrational analysis was performed at the stationary points and the harmonic vibrational frequencies were calculated with the second derivatives numerically computed from the analytical first derivatives. The zero-point energy correction was performed for calculating the adiabatic excitation energies, $T_0$. In the present results, all of the geometrical parameters are given as $r_e$ and $\theta_e$, not as $r_0$ and $\theta_0$.

The ground and valence excited states of triatomic monohydrides with singlet and triplet spin multiplicities were calculated; namely, the ground, singlet, and triplet excited states ($^1\Sigma^+, ^1\Pi^+, ^3\Pi^+$) of HCX (X = F, Cl), HSIX (X = F, Cl), and HAO (A = N, P). The basis set dependence of the equilibrium geometries and $T_0$ was examined for HSIF with Dunning’s correlation-consistent polarized valence double zeta (cc-pVDZ), cc-pVTZ, and cc-pVQZ basis sets,\textsuperscript{31} without f- and g-type polarization functions for Si and F and without d- and f-type polarization functions for H. These basis sets are denoted as cc-pVTZ-\textit{f} and cc-pVQZ-\textit{f},\textit{g} in the present paper. The basis set examination showed that cc-pVTZ-\textit{f} provides reasonable results at an acceptable computational cost and, therefore, the calculations of other molecules were performed with the cc-pVTZ-\textit{f} basis sets \{4s3p2d3s2p5s5p4d2d\}.

In the SAC–CI calculations, the direct algorithm of the SAC–CI SD–R method\textsuperscript{14} has been utilized without perturbation selection of the linked operators to calculate the valence excited states. The SD–R method has been shown to describe the excited states accurately when the excited states are predominantly described by one-electron processes. The recently developed direct SAC–CI method enables accurate and efficient calculations. This direct SAC–CI method calculates all the product terms of $S_2S_3$, $S_2R_1$, and $S_2R_3$ without selection, where $S_2$ denotes linked double operators in SAC and $R_1$ and $R_3$ are linked single and double operators in SAC–CI, respectively. All of the direct SAC–CI calculations were performed by the nonvariational method, which is the default in...
the program system. Recently, the analytical energy gradients of the direct SAC–CI method have also been developed and implemented.

To reduce the computational cost of calculating the ground- and excited-state geometries and harmonic vibrational frequencies, a method incorporating perturbation selection has been examined. The LMOs calculated by Pipek–Mezey population localization were used. The MOD selection has been examined. The LMOs calculated by Pipek–Mezey population localization were used. The MOD selection has been examined. The LMOs calculated by Pipek–

For evaluating the anharmonic vibrational frequencies, the 3D PESs were calculated around the local minima with 343 geometric points (seven cubic points) to cover the region of the 3D vibrational wavefunctions. The 3D PESs were described in the binding coordinates \((r_1, r_2, \theta)\), where \(r_1\) and \(r_2\) are the bond distances and \(\theta\) defines the bond angle. For calculating the vibrational wavefunctions, these energy points were fitted with the 3D fifth-order Morse–cosine function,

\[
V(r_1, r_2, \theta) = \sum_{i,j,k=0} B_{ijk} \left( 1 - e^{-\alpha(r_i-r_e)} \right)^j \times \left( 1 - e^{-\alpha(r_j-r_e)} \right)^k (\cos \theta - \cos \theta_e)^k, \tag{1}
\]

where \(r_e\) and \(\theta_e\) are the equilibrium values. The linear parameters \(\{ B_{ijk} \}\) were obtained by a least-square fitting with varying of the nonlinear parameters \((\alpha_i, \alpha_j)\). The fitting of the 3D PES was satisfactory and the mean deviation from the \(ab initio\) values at 343 geometric points was 0.1–0.6 cm\(^{-1}\) for all the electronic states of the present molecules. This 3D PES expansion guarantees accurate calculations of the vibrational energy levels and wavefunctions, including anharmonicity.

For simulating the vibrational spectrum, 3D vibrational states were calculated by the grid method, in which the Lanczos algorithm was adopted for the diagonalization. In the binding coordinates, the kinetic part of the Hamiltonian \((J = 0)\) of the vibrational motion of the A–B–C system is given by

\[
T = \frac{p_1^2}{2 \mu_{AB}} + \frac{p_2^2}{2 \mu_{BC}} + \frac{j^2}{2 \mu_{BC}^2} + \frac{j^2}{2 \mu_{AB}^2} + \frac{p_1 p_2 \cos \theta}{m_B} \tag{2}
\]

where

\[
p_k = -i \frac{\partial}{\partial r_k}, \quad k = 1, 2, \quad p_\theta = -i \frac{\partial}{\partial \theta} \sin \theta \quad \text{and} \quad j^2 = - \sin \theta \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta}. \tag{3}
\]

and \(\mu_{AB}\) and \(\mu_{BC}\) are the reduced masses of the A–B and B–C systems, respectively. The coordinates \(r_1\) and \(r_2\) are represented by the Hermite discrete variable representation (DVR) with 30 points and \(\theta\) by the Legendre DVR of 19 points. Thus, the 3D vibrational wavefunction is represented at the grid points,

\[
x_j(x) = (2^j j! \mu_{AB} \mu_{BC})^{1/4} H_j(\sqrt{\mu_{AB} \mu_{BC}}(x - \bar{x})) e^{-\mu_{AB} \mu_{BC} (x - \bar{x})^2/2}, \tag{4}
\]

\[
x_{l,m+1}(\theta) = \sqrt{\frac{2l + 1}{(l + m)!}} \frac{\sin l \theta}{(l + m)!} P_m^l \cos(\theta). \tag{5}
\]

The FC factors were calculated using the 3D vibrational wavefunctions.

The SAC/SAC–CI calculations were conducted using the GAUSSIAN09 suite of programs, Revision B.01. The vibrational wavefunctions were calculated with the MCTDH program package, version 8.3.

III. VALENCE EXCITED STATES

A. Structure of HAX (A = C, Si; X = F, Cl) in the ground and excited states

First, the equilibrium structures of the \(X^1A^1, A^1A^\prime\), and \(A^1A^\prime\) states of HSiF, whose valence electronic structure in the ground state is \((8a')^2(2a'')^2(0a')^2(10a')^2(3a'')^2\), have been calculated to examine the basis set dependence for the geometrical parameters and adiabatic excitation energies \((T_0)\). The cc-pVDZ, cc-pVTZ–f, and cc-pVQZ–f basis sets have been examined and the results are compared in Table I together with the available experimental values. The ground-state structure was obtained as \(r_{HSi} = 1.526\ \text{Å}, r_{SF} = 1.616\ \text{Å}, \) and \(\theta = 96.7^\circ\) with cc-pVQZ–f in good agreement with the experimental values of \(r_{HSi} = 1.528\ \text{Å}, r_{SF} = 1.603\ \text{Å}, \) and \(\theta = 96.9^\circ\), respectively. The low-lying excited states, \(A^1A^\prime\) and \(A^1A^\prime\), are characterized as a 10a’ \(\rightarrow\) 3a’ transition that is \(n\pi^*\) in character. In the excited states, the prominent geometry change occurs in the bond angle; the bond angle of \(A^1A^\prime\) is enlarged to 115.2°, which is also in good agreement with the experimental value of 115.0°. The bond lengths in the \(A^1A^\prime\) state were predicted to shrink, in agreement with experiment. The calculated \(T_0\) of the \(A^1A^\prime\) state is 2.974 eV compared with the experimental value of 2.884 eV. The agreement with the experimental values in both geometrical parameters and \(T_0\) generally improves as the quality of the basis set improves. For the \(a^1A^\prime\) state, a large geometry change from the ground state has also been calculated for the bond angle \((114.2^\circ)\) and the \(r_{HSi}\) bond length \((1.484\ \text{Å})\). The bond angle in \(a^1A^\prime\) is similar to that in \(A^1A^\prime\), while \(r_{HSi}\) in \(a^1A^\prime\) is much shorter than \(r_{HSi}\) in \(A^1A^\prime\). This state has been calculated to be located at 1.612 eV relative to the ground state. Unfortunately, there are no experimental data for this state. The results using the cc-pVTZ–f basis set are also satisfactory compared with those using the cc-pVQZ–f basis set; the deviations are \(<0.012\ \text{Å}\) in bond length, \(<0.4^\circ\) in bond angle, and \(<0.013\ \text{eV}\) in \(T_0\) for the ground and excited states of HSiF, as in Table I. The moderate deviation of the calculated \(r_{SF}\) values from the experimental ones can be partly attributed to the slow convergence of electron correlation with respect to angular momentum in the basis set; f and g functions were not included in the present calculations.
TABLE I. Geometries and adiabatic excitation energies (eV) of HSiF calculated by the direct SAC–CI SD–R method; basis set dependence.

<table>
<thead>
<tr>
<th>State</th>
<th>Method</th>
<th>Basis set</th>
<th>( r_{HSi} ) (Å)</th>
<th>( r_{SiF} ) (Å)</th>
<th>( \theta ) (°)</th>
<th>( T_0 )</th>
<th>( \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X^1A' )</td>
<td>SAC</td>
<td>cc-pVDZ</td>
<td>1.540</td>
<td>1.664</td>
<td>96.7</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cc-pVTZ-f</td>
<td>1.533</td>
<td>1.626</td>
<td>96.7</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cc-pVQZ-f</td>
<td>1.526</td>
<td>1.616</td>
<td>96.7</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
</tr>
<tr>
<td></td>
<td>Expt. (( r_{e}, \theta_{e} ))</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
<td></td>
</tr>
<tr>
<td>( X^2A'' )</td>
<td>SAC–CI</td>
<td>cc-pVDZ</td>
<td>1.548</td>
<td>1.670</td>
<td>113.8</td>
<td>3.037</td>
<td>( \ldots )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cc-pVTZ-f</td>
<td>1.533</td>
<td>1.625</td>
<td>114.8</td>
<td>3.000</td>
<td>( \ldots )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cc-pVQZ-f</td>
<td>1.522</td>
<td>1.613</td>
<td>115.2</td>
<td>2.974</td>
<td>( \ldots )</td>
</tr>
<tr>
<td></td>
<td>Expt. (( r_{e}, \theta_{e} ))</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
<td></td>
</tr>
<tr>
<td>( a^1A'' )</td>
<td>SAC–CI</td>
<td>cc-pVDZ</td>
<td>1.498</td>
<td>1.664</td>
<td>114.6</td>
<td>1.637</td>
<td>( \ldots )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cc-pVTZ-f</td>
<td>1.491</td>
<td>1.622</td>
<td>114.1</td>
<td>1.625</td>
<td>( \ldots )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cc-pVQZ-f</td>
<td>1.484</td>
<td>1.619</td>
<td>114.2</td>
<td>1.612</td>
<td>( \ldots )</td>
</tr>
</tbody>
</table>

\( ^a \) cc-pVTZ-f and cc-pVQZ-f denotes cc-pVTZ/QZ basis sets without f and g functions for Si and F and without d and f functions for H.

Because the calculations with cc-pVTZ–f have provided relatively well-converged results in the basis set examination for HSiF, we performed the calculations of the spectroscopic constants of other molecules with the cc-pVTZ–f basis set. The results for the geometric parameters for the \( X^1A', A^1A'', \) and \( a^1A'' \) states of HAX (\( A = C, Si; X = F, Cl \)) with the cc-pVTZ–f basis set are summarized in Table II comparing with other theoretical and experimental values. Because these four molecules have isovalence electronic structures, the geometry changes in the excited states are similar; the HA and AX bond lengths shrink and the bond angle becomes larger in the excited states. For HCF, Schmidt et al. determined the spectroscopic constants of the \( X^1A', A^1A'', \) and \( a^1A'' \) states using multireference configuration interaction (MRCI) calculations with cc-pVTZ and cc-pVQZ followed by Davidson correction.\(^{25}\) The present SAC–CI calculation provides results of similar quality to the MRCI calculation compared with the experimental values of the \( X^1A' \) (Ref. 36) and \( A^1A'' \) states;\(^{37,38}\) the deviations from experimental values are within 0.03 Å for \( r_{HCX} \), 0.004 Å for \( r_{CSi} \), and 0.8° for \( \theta \). For \( a^1A'' \), the SAC–CI calculation also supported the previous calculation; for example, the bond angle is smaller than that of \( A^1A'' \).\(^{35}\) The calculated \( T_0 \) values of the \( A^1A'' \) and \( a^1A'' \) states are 2.215 and 0.542 eV, respectively, and the experimental value of \( A^1A'' \) is 2.142 eV. For HCCI, although experimental\(^{39,40}\) and other theoretical\(^{26,27}\) works have been reported, information on the \( A^1A'' \) and \( a^1A'' \) states is limited. The present SAC–CI method has calculated the adiabatic excitation energy of the \( A^1A'' \) state as 1.607 eV compared with the observed value of \( T_0 = 1.524 \) eV.\(^{40}\) The \( a^1A'' \) state is located very close to the ground \( X^1A' \) state (\( T_0 = 0.149 \) eV). A MP2 study has been reported for the \( X^1A' \) and \( a^1A'' \) states.\(^{26}\) Our results are similar to the MP2 values for bond angle; however, the CCl bond distance is longer by 0.017 Å. For HSiF, the present calculation has yielded satisfactory results compared with the experimental values\(^{19,23}\) as discussed above and gave results of similar quality to the CCSD(T) with aug-cc-pVQZ for \( X^1A' \) and the complete-active-space self-consistent-field (CASSCF)/MRCI with aug-cc-pVQZ for \( A^1A'' \).\(^{23}\) This means the effect of the triple correction is small for the ground-state geometrical parameters of this molecule. The present calculations also gave excellent results for HSiCl; deviations from the experimental values\(^{22,41}\) are within 0.01 Å for \( r_{HSi} \), 0.04 Å for \( r_{SiCl} \), and 0.6° for \( \theta \) for the \( X^1A' \) and \( A^1A'' \) states. For the \( A^1A'' \) states, density functional theory calculations with B3LYP/6–311G(3df,3pd) also gave results of similar quality. The calculated \( T_0 \) of \( A^1A'' \) was 2.679 eV compared with the experimental value of 2.569 eV.

Thus, in the present calculations, for the halocarbenes and halosilenes (HAX), the agreement with the experimental values for the \( X^1A' \) and \( A^1A'' \) states is satisfactory; the average discrepancies of the geometric parameters between theoretical and available experimental values are 0.012 Å, 0.022 Å, and 0.4° for \( r_{HSi} \), \( r_{CSi} \), and \( \theta \), respectively. The adiabatic excitation energies have also been well reproduced; the mean deviation from the experimental values is 0.096 eV. Because these excited states are described by one-electron processes, the SD–R method describes these excited states satisfactorily. The less accurate results in bond lengths (\( r_{AX} \)), in particular for HSiF and HSiCl, can be attributed to the quality of the basis set. As we have demonstrated for HSiF in Table I, the higher basis set such as cc-pVQZ-f,g improves the results, however, the systematic calculations including vibrational frequency are practically too expensive with higher basis sets.

The geometry change in the excited states can be qualitatively interpreted with the ESF theory.\(^{29}\) Because the geometry changes in the excited states of HCX and HSiX are similar, the changes in HSiF have been analyzed. The MOs related to the transition are shown in Fig. 1. Figure 2 shows the contour plot of the electron density difference between the \( X^1A' \) and \( A^1A'' \) states in the molecular plane (\( \sigma_y \) plane), where the effective density matrices (EDMs) of the SAC/SAC–CI energy gradients were used with the cc-pVTZ–f basis at the ground-state geometry. The contour value denotes EDM(\( A^1A'' \))–EDM(\( X^1A' \)) and, therefore, the negative value means that the electron density is reduced because of the electron excitation. As mentioned above, in the \( A^1A'' \) state, the prominent geometry change occurs in the bond angle; \( \theta = 96.7° \) in \( X^1A' \) is enlarged to \( \theta = 114.8° \) in \( A^1A'' \). Figures 1 and 2 show that the \( n^* \) transition reduces an atomic dipole (AD) force in the molecular plane acting on the Si atom, which causes the bond angle to increase. A similar electron density change occurs in the \( a^1A'' \) state and also in the excited states of the other molecules.
TABLE II. Geometries and adiabatic excitation energies (eV) of HAX (A = C, Si; X = F, Cl) calculated by the direct SAC–CI SD–R method with cc-pVTZ–f basis sets. The uncertainty in a structural parameter given in parentheses applies to the last significant figures.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>State</th>
<th>Method</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>(r_{HA}) (Å)</td>
</tr>
<tr>
<td>HCF</td>
<td>(X^1A')</td>
<td>MRCI+Dav. (^a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SAC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expt. ((\epsilon_r, \epsilon_\theta)) (^b)</td>
</tr>
<tr>
<td></td>
<td>(A^1A'')</td>
<td>MRCI+Dav. (^a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SAC–CI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expt. ((\epsilon_r, \epsilon_\theta)) (^c)</td>
</tr>
<tr>
<td></td>
<td>(\alpha^3A'')</td>
<td>MRCI+Dav. (^a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SAC–CI</td>
</tr>
<tr>
<td>HCCI</td>
<td>(X^1A')</td>
<td>MP2 (^e)</td>
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<tr>
<td></td>
<td></td>
<td>SAC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expt. ((\epsilon_r, \epsilon_\theta)) (^f)</td>
</tr>
<tr>
<td></td>
<td>(A^1A'')</td>
<td>SAC–CI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expt. (^g)</td>
</tr>
<tr>
<td></td>
<td>(\alpha^3A'')</td>
<td>MP2 (^e)</td>
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<tr>
<td></td>
<td></td>
<td>SAC–CI</td>
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<td>HSiF</td>
<td>(X^1A')</td>
<td>CCSD(T) (^h)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SAC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expt. ((\epsilon_r, \epsilon_\theta)) (^i)</td>
</tr>
<tr>
<td></td>
<td>(A^1A'')</td>
<td>CASSCF/MRCI (^h)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SAC–CI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expt. ((\epsilon_r, \epsilon_\theta)) (^i)</td>
</tr>
<tr>
<td></td>
<td>(\alpha^3A'')</td>
<td>SAC–CI</td>
</tr>
<tr>
<td>HSiCl</td>
<td>(X^1A')</td>
<td>DFT (^j)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SAC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expt. ((\epsilon_r, \epsilon_\theta)) (^k)</td>
</tr>
<tr>
<td></td>
<td>(A^1A'')</td>
<td>DFT (^j)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SAC–CI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expt. ((\epsilon_r, \epsilon_\theta)) (^k)</td>
</tr>
<tr>
<td></td>
<td>(\alpha^3A'')</td>
<td>SAC–CI</td>
</tr>
</tbody>
</table>

Mean deviations from expt.

\(^a\)Reference 25.
\(^b\)Reference 36.
\(^c\)Reference 37.
\(^d\)Reference 38.
\(^e\)Reference 26.
\(^f\)Reference 39.
\(^g\)Reference 40.
\(^h\)Reference 23.
\(^i\)Reference 19.
\(^j\)Reference 22.
\(^k\)Reference 41.

B. Harmonic and anharmonic vibrational frequencies of HAX (A = C, Si; X = F, Cl)

The vibrational frequencies of HAX (A = C, Si; X = F, Cl) and their deuterium isotopomers have been investigated. In Table III, the calculated harmonic (\(\omega\)) and anharmonic (\(\nu\)) vibrational frequencies of the \(X^1A', A^1A'',\) and \(\alpha^3A''\) states of the HAX molecules are compared with the experimental \(^{19,21,36,42-44}\) and other theoretical values. The high-resolution vibrational spectra of the \(X^1A'\) and \(A^1A''\) states of HSiX (X = F, Cl) were measured by single vibronic level emission spectroscopy and the harmonic frequencies were extracted. \(^{20,22,23}\) For the harmonic frequencies, the present theoretical values show reasonable agreement with...
the experimental values; the deviations from the experimental values are 5–24 cm\(^{-1}\) and 0–19 cm\(^{-1}\) for HSiF and HSiCl, respectively. In HSiF, the harmonic frequency of the bending coordinate \(\omega_2\) becomes smaller in both the \(A^1A^1\) (592 cm\(^{-1}\), expt. 597 cm\(^{-1}\)) and \(a^3A^1\) (691 cm\(^{-1}\)) states compared with the \(X^1A^1\) state (881 cm\(^{-1}\), expt. 876 cm\(^{-1}\)); the PESs of the excited states become flat in this coordinate because the AD force decreases. In the \(A^1A^1\) state, \(\omega_2\) is drastically reduced (1797 cm\(^{-1}\)), but \(\omega_3\) does not change so much (844 cm\(^{-1}\)), which agrees well with the experimental observation (\(\omega_1 = 1816\) and \(\omega_3 = 868\) cm\(^{-1}\)).\(^{19}\) In the \(a^3A^1\) state, on the other hand, both \(\omega_1\) and \(\omega_3\) have been predicted to become larger than those of the \(X^1A^1\) state and \(\omega_2\) is reduced, as in the \(A^1A^1\) state. For HSiCl, the same trend as seen in HSiF has been observed in the calculated harmonic frequencies. The calculated harmonic frequencies of HSiCl show good agreement with the experimental values for the \(X^1A^1\) (Ref. 22) and \(A^1A^1\) states;\(^{22,41}\) the mean deviation from the experimental values was \(\sim 10\) cm\(^{-1}\).

The trend in the anharmonic vibrational frequencies of these electronic states is similar to those of the harmonic frequencies. The anharmonicity of the vibrational frequencies is large in the stretching \(v_1\) (HSi) mode in both the ground and excited states of HSiX. For example, the calculated vibrational fundamental frequencies, \(v_1\), of HSiF are 1928 and 1566 cm\(^{-1}\) for the \(X^1A^1\) and \(A^1A^1\) states, respectively; the deviations from the harmonic values \(\omega_1\) are 75 and 231 cm\(^{-1}\), respectively. The PESs in the bending coordinate are flat and the vibrational frequencies of \(v_2\) are as small as 557 cm\(^{-1}\) (expt. 558 cm\(^{-1}\)) for the \(A^1A^1\) state, which indicates that accurate analysis with the 3D PESs is necessary for evaluating the anharmonicity. In both HSiF and HSiCl, the agreement of the vibrational frequencies with the observed values is satisfactory; the average deviations from the available experimental values are \(\sim 11\) cm\(^{-1}\) for the \(X^1A^1\) and \(A^1A^1\) states of HSiF and HSiCl.

For halocarbenes, the fundamental vibrational frequencies have been reported for the ground states of HCF and HCCI.\(^{36,43}\) The present calculation provided satisfactory results; for example, the calculated vibrational frequencies of the \(X^1A^1\) state of HCF are 2655 (\(v_1\)), 1424 (\(v_2\)), and 1205 (\(v_3\)) cm\(^{-1}\) compared with the observed values of 2643, 1403, and 1204 cm\(^{-1}\), respectively. Experimental studies of the excited-state vibrational frequencies for these molecules, on the other hand, are limited; only the \(v_2\) values of \(A^1A^1\) observed in the UV spectra have been reported for HCF and HCCI because the vibrational progression is large in this coordinate. The present calculation also reproduced the \(v_2\) values of the \(A^1A^1\) state satisfactorily; the calculated values are 1022 and 882 cm\(^{-1}\) for HCF and HCCI, respectively.
compared with the experimental values of 1021 and 865 cm\(^{-1}\). As for the spectroscopic parameters of HCF, MRSDCI calculations with extended basis sets have been reported for the \(X^1\) \(A\)^\(^1\), \(A^1\) \(A\)^\(^1\), and \(a^1\) \(A\)^\(^1\) states. From the viewpoint of the harmonic frequencies, the present SAC–CI values show good agreement with those by the MRCl calculation.\(^{25}\) Comparing the present harmonic values with the vibrational frequencies, the anharmonicity is also significant for \(v_1\) in the ground and excited states of HCX, as in HSIX. The vibrational frequencies of the bending coordinate, \(v_2\), are reduced in both the \(A^1\) \(A\)^\(^1\) and \(a^1\) \(A\)^\(^1\) states.

The vibrational frequencies of DCX (\(X = F, Cl\)) and DSIX (\(X = F, Cl\)) have also been calculated using the same 3D PESs of HAX; the Born–Oppenheimer (BO) approximation being adopted. The calculated vibrational frequencies are summarized in Table IV together with the experimental values. The trend in the vibrational frequencies of the ground and excited states is the same as those of the HAX molecules in which the BO approximation was adopted. For halocarbenes (DCF and DCCI), the experimental values of the bending mode have been reported. The calculated \(v_2\) values of 1078 and 790 cm\(^{-1}\) for \(X^1\) \(A\)^\(^1\) and \(A^1\) \(A\)^\(^1\) states of DCF compare well with the experimental values of 1046 and 780 ± 5 cm\(^{-1}\), respectively. For DSIF and DSICI, high-resolution emission spectroscopy has been applied to provide accurate vibrational levels of the ground state. The present values for \(X^1\) \(A\)^\(^1\) of DSIF, 1401 (\(v_1\)), 642 (\(v_2\)), and 831 (\(v_3\)) cm\(^{-1}\), are in excellent agreement with the experimental values, 1401 (\(v_1\)), 638 (\(v_2\)), and 840 (\(v_3\)) cm\(^{-1}\), respectively. The vibrational frequencies of the excited states of DSIF and DSICI have not been well studied experimentally.

### C. Vibrational level emission and absorption spectra

The calculated vibrational energies of the lowest 20 vibrational levels and their assignments for HSIF and DSIF are summarized in Table V. Those of other molecules (HCF, HCCl, and HSICI) and their deuterium isotopomers (DCF, DCCI, and DSICI) are compiled in the supplementary material of Tables S1–S3.\(^{45}\) Not all of the vibrational levels were measured in the high-resolution spectrum\(^{19,20}\) because the vibrational levels in the stretching modes (\(v_1\), \(v_3\)) are not very excited. These data may help in the detailed assignment in future analyses.

The vibrational spectra in the electronic transition are sensitive to the relative positions of the potential minima in the ground and excited states and the shape of the PESs, which is of interest for the present examination of the accuracy of the SAC/SAC–CI calculation. The SAC/SAC–CI describes the well-balanced PESs of the ground and excited states. Because the high-resolution vibronic level emission spectra have been reported for HSIF and DSIF\(^{19,20}\) the vibrational spectra were simulated for these molecules based on the calculated 3D PESs. Theoretical simulations have also been performed previously.\(^{23,24}\) The calculated vibrational emission spectra from the \(A\)(000) and \(A\)(110) levels of HSIF and those from the \(A\)(000) and \(A\)(010) levels of DSIF within the FC approximation are compared with the experimental spectra in Figs. 3 and 4, respectively. The present theoretical spectra satisfactorily reproduce the experimental spectra in both peak position and relative intensity of the vibrational progression. The \(A\)(010) and \(A\)(110) levels of HSIF are the second and tenth vibrational states; therefore, complex vibrational structures are observed. The present SAC–CI calculations have provided reliable results not only for the main progression based on the bending mode, but also for the small structure due to the stretching modes, as seen in Fig. 3. In the \(A\)(010) emission spectra, transitions to the \((000)\) and \((010)\) have large FC factors and the progression of higher \((0n0)\) levels is seen with the peak maximum of \((050)\). This trend agrees well with the experimental spectrum. In the \(A\)(110) emission spectra, the transitions overlap and the peaks are assigned as shown in Fig. 3; each peak has two dominant contributions except for \((100)\) and \((200)\) peaks. This feature was not seen in previous work.\(^{20,23}\) The \((000)\) and \((010)\) levels of DSIF are the vibrational ground and first excited states. In the spectra, to cover the energy region of 0–5500 cm\(^{-1}\), calculations up to \(\sim 70\) vibrational states are necessary. The simulated vibrational spectra are also in excellent agreement with the experimental spectra. The \((000)\) emission spectrum has a maximum intensity at the \((020)\) level. The \((010)\) emission spectrum of DSIF is similar to that of HSIF and the peak maximum in the higher levels is at \((060)\), which agrees well with the experimental spectrum. The vibrational progressions in the spectra of both HSIF and DSIF are predominantly due to the bending mode and the structure resulting from the stretching modes is less prominent because the geometry changes are large in the bending mode.

### Table IV. Vibrational frequencies of the ground and excited states of DAX (\(A = C, Si; X = F, Cl\)) calculated by the SAC–CI SD-R method with cc-pVTZ-f basis sets.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>State</th>
<th>Method</th>
<th>(v_1)(HA)</th>
<th>(v_2)(bend)</th>
<th>(v_3)(AX)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCF</td>
<td>(X^1)(A)^(^1)</td>
<td>SAC</td>
<td>1964</td>
<td>1078</td>
<td>1209</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expt. (Ar)(^{a})</td>
<td>...</td>
<td>1046</td>
<td>1183</td>
</tr>
<tr>
<td></td>
<td>(A^1)(A)^(^1)</td>
<td>SAC–CI</td>
<td>2024</td>
<td>790</td>
<td>1250</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expt. (gas)(^{b})</td>
<td>...</td>
<td>780(5)</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>(a^1)(A)^(^1)</td>
<td>SAC–CI</td>
<td>2244</td>
<td>865</td>
<td>1231</td>
</tr>
<tr>
<td>DCCI</td>
<td>(X^1)(A)^(^1)</td>
<td>SAC</td>
<td>2086</td>
<td>913</td>
<td>775</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expt. (gas)(^{a})</td>
<td>...</td>
<td>805</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>(A^1)(A)^(^1)</td>
<td>SAC–CI</td>
<td>2249</td>
<td>669</td>
<td>868</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expt. (Ar)(^{a})</td>
<td>...</td>
<td>657</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>(a^1)(A)^(^1)</td>
<td>SAC–CI</td>
<td>2274</td>
<td>728</td>
<td>850</td>
</tr>
<tr>
<td>DSIF</td>
<td>(X^1)(A)^(^1)</td>
<td>SAC</td>
<td>1401</td>
<td>642</td>
<td>831</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expt. (gas)(^{b})</td>
<td>1401</td>
<td>638</td>
<td>840</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expt. (Ar)(^{a})</td>
<td>1387</td>
<td>638</td>
<td>833</td>
</tr>
<tr>
<td></td>
<td>(A^1)(A)^(^1)</td>
<td>SAC–CI</td>
<td>1178</td>
<td>424</td>
<td>829</td>
</tr>
<tr>
<td></td>
<td>(a^1)(A)^(^1)</td>
<td>SAC–CI</td>
<td>1493</td>
<td>506</td>
<td>847</td>
</tr>
<tr>
<td>DSICI</td>
<td>(X^1)(A)^(^1)</td>
<td>SAC</td>
<td>1434</td>
<td>594</td>
<td>503</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expt.(gas)(^{b,d})</td>
<td>(1473)</td>
<td>(601)</td>
<td>(525)</td>
</tr>
<tr>
<td></td>
<td>(A^1)(A)^(^1)</td>
<td>SAC–CI</td>
<td>1297</td>
<td>406</td>
<td>522</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expt.(gas)(^{a})</td>
<td>...</td>
<td>409</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>(a^1)(A)^(^1)</td>
<td>SAC–CI</td>
<td>1447</td>
<td>452</td>
<td>550</td>
</tr>
</tbody>
</table>

\(^{a}\)Reference 42.

\(^{b}\)Reference 22.

\(^{c}\)Reference 44.

\(^{d}\)Values in the parentheses are harmonic vibrational frequencies.
TABLE V. Vibrational levels \((\nu_1, \nu_2, \nu_3)\) of HSiF and DSiF calculated by the SAC–CI 3-D PESs. Energy \((E)\) is given in cm\(^{-1}\).

<table>
<thead>
<tr>
<th>No.</th>
<th>State (X^1A')</th>
<th>(E)</th>
<th>State (A^1A'')</th>
<th>(E)</th>
<th>State (a^3A'')</th>
<th>(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(000)</td>
<td>0</td>
<td>(000)</td>
<td>0</td>
<td>(000)</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>(001)</td>
<td>829</td>
<td>(010)</td>
<td>557</td>
<td>(010)</td>
<td>674</td>
</tr>
<tr>
<td>3</td>
<td>(010)</td>
<td>867</td>
<td>(001)</td>
<td>832</td>
<td>(001)</td>
<td>849</td>
</tr>
<tr>
<td>4</td>
<td>(002)</td>
<td>1650</td>
<td>(020)</td>
<td>1103</td>
<td>(020)</td>
<td>1343</td>
</tr>
<tr>
<td>5</td>
<td>(011)</td>
<td>1692</td>
<td>(011)</td>
<td>1385</td>
<td>(011)</td>
<td>1519</td>
</tr>
<tr>
<td>6</td>
<td>(020)</td>
<td>1729</td>
<td>(100)</td>
<td>1566</td>
<td>(002)</td>
<td>1689</td>
</tr>
<tr>
<td>7</td>
<td>(010)</td>
<td>1928</td>
<td>(002)</td>
<td>1637</td>
<td>(030)</td>
<td>2006</td>
</tr>
<tr>
<td>8</td>
<td>(003)</td>
<td>2463</td>
<td>(030)</td>
<td>1654</td>
<td>(002)</td>
<td>2043</td>
</tr>
<tr>
<td>9</td>
<td>(012)</td>
<td>2510</td>
<td>(021)</td>
<td>1927</td>
<td>(021)</td>
<td>2185</td>
</tr>
<tr>
<td>10</td>
<td>(021)</td>
<td>2551</td>
<td>(110)</td>
<td>2067</td>
<td>(021)</td>
<td>2356</td>
</tr>
<tr>
<td>11</td>
<td>(003)</td>
<td>2585</td>
<td>(012)</td>
<td>2157</td>
<td>(003)</td>
<td>2521</td>
</tr>
<tr>
<td>12</td>
<td>(011)</td>
<td>2756</td>
<td>(040)</td>
<td>2204</td>
<td>(040)</td>
<td>2660</td>
</tr>
<tr>
<td>13</td>
<td>(010)</td>
<td>2782</td>
<td>(011)</td>
<td>2394</td>
<td>(011)</td>
<td>2695</td>
</tr>
<tr>
<td>14</td>
<td>(004)</td>
<td>3267</td>
<td>(031)</td>
<td>2457</td>
<td>(031)</td>
<td>2844</td>
</tr>
<tr>
<td>15</td>
<td>(013)</td>
<td>3319</td>
<td>(012)</td>
<td>2468</td>
<td>(012)</td>
<td>2891</td>
</tr>
<tr>
<td>16</td>
<td>(012)</td>
<td>3365</td>
<td>(022)</td>
<td>2553</td>
<td>(022)</td>
<td>3018</td>
</tr>
<tr>
<td>17</td>
<td>(021)</td>
<td>3438</td>
<td>(050)</td>
<td>2742</td>
<td>(050)</td>
<td>3305</td>
</tr>
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<td>18</td>
<td>(030)</td>
<td>3577</td>
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<td>2888</td>
<td>(004)</td>
<td>3342</td>
</tr>
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<td>(111)</td>
<td>3606</td>
<td>(013)</td>
<td>2919</td>
<td>(120)</td>
<td>3344</td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The vibrational structure in the absorption spectrum shows vibrational levels in the excited states that are also of particular interest in the present study. The LIF spectra of HSiCl and DSiCl molecules were measured for the \(X^1A'\)–\(A^1A''\) transition.\(^\text{21}\) Recently, highly accurate calculations of the vibrational level absorption spectra of these molecules were performed using the RCCSD(T) and CASSCF/MRCI methods.\(^\text{24}\) In this simulation, they also considered the thermal distribution in the ground state at 300 K. In the present calculation, we focus on the vibrational level absorption spectra from the vibrational ground state and do not include the thermal effect. In Fig. 5, the vibrational level absorption spectra of HSiCl and DSiCl are compared with the observed SVL emission spectra (Ref. 20). The present SAC–CI vibrational level absorption spectra agree well with those in the experimental LIF spectra\(^\text{21}\) and the previous calculations.\(^\text{24}\) In the spectra of HSiCl, the vibrational progression of the bending mode is predominant and the FC factors for \(2^1_1\) and \(2^2_0\) are large. The FC factors for other vibrational states, \(3^1_0, 3^2_0, 2^1_1, 2^3_0\), were calculated to be small. The thermal state in the ground state, \(1^1_{10}, 1^1_{20}, 1^2_{10}, 1^2_{20}\), measured in the LIF spectra are not considered in the present calculation. The present calculation also reproduced the vibrational structure in the absorption LIF spectra of DSiCl. The vibrational progression in the bending mode, \(2^1_0, 2^2_0\), is prominent and the FC factors of the \(2^1_0, 2^2_0, 2^3_0\) transitions are also large. Comparing low-lying peaks, the order of some peaks is different between HSiCl and DSiCl. For example, the peak \(2^1_0\) is below \(3^1_0\) in DSiCl while their order is reversed in HSiCl. This is because the vibrational frequency \(\nu_3\) is smaller than \(\nu_2\) in HSiCl and the isotope effect is significant in bending coordinate \((\nu_2)\); but is small in stretching coordinate \((\nu_3)\) and therefore, the order of these peaks is reversed between HSiCl and DSiCl. The detailed vibrational energy levels of HSiCl...
FIG. 4. The SAC–CI A(000) and A(010) emission spectra of DSiF compared with the observed SVL emission spectra (Ref. 20).

and DSiCl are compiled in Table S3 of the supplementary material.45

The present simulations of the vibronic level emission and absorption spectra show that the SAC/SAC–CI PESs are accurate and well balanced in the ground and excited states.

D. HNO and HPO

The HNO and HPO molecules also have isovalence electronic structures to HSiF; the valence electronic structure of HNO in the ground state is \( \ldots (6a')^2(1a')^2(7a')^2(3a'')^0 \). The results of the geometrical parameters and adiabatic excitation energies in the ground and singlet/triplet excited states of these molecules are summarized in Table VI with the experimental values.42, 46, 47 and previous theoretical results.28, 48 Luna et al.28 investigated these electronic states by CASPT2 with the extensive ANO-type basis set \([6s5p4d3f/5s4p3d2f/3s2p1d]\). For \( T_0 \) of the \( A^1A'' \) state, the SAC–CI calculations with cc-pVTZ–f have provided excellent values of 1.646 and 2.346 eV for HNO and HPO, respectively, in comparison with experimental values of 1.631 (Ref. 46) and 2.360 eV.47 The CASPT2 calculation28 underestimated these energies by about 0.2 eV. For \( T_0 \) of the \( a^3A'' \) state, the present calculations have underestimated the experimental value by about 0.07 eV for HNO and have yielded a lower value for HPO compared with the QCISD(T) calculation with 6–311+G(3df,2p).48

For the geometry changes in the \( A^1A'' \) and \( a^3A'' \) states, the present calculations support the CASPT2 results. The calculated bond-angle change of the \( A^1A'' \) state is different between these two molecules; the bond angle of HPO decreases, in contrast to other molecules with this isovalence electronic structure. Although the experimental bond angle is 105.0° for \( A^1A'' \), theories predicted smaller angles of 93.3° by SAC–CI and 95.3° by CASPT2.28 For \( a^3A'' \), the calculated bond angles are larger at 118.1° and 110.3° for HNO and HPO, respectively. The geometry changes in bond distances of HNO and HPO are also different from those of HCX and HSiX (X = F, Cl). The NO (PO) bond is elongated in \( A^1A'' \) by +0.03 (+0.09) Å, in reasonable agreement with the experiment and the previous CASPT2 calculation. This feature of the bond-distance change has also been found in the \( a^3A'' \) state.

The harmonic vibrational frequencies of these states have also been calculated and summarized in Table VII with other theoretical28 and experimental values.42, 46, 47
the CASPT2 calculations, the vibrational frequencies were evaluated by the second-degree polynomial fitting of the PESs. The experimental values are fundamental vibrational frequencies and, therefore, theoretical vibrational frequencies including anharmonicity can be compared. In HNO, the ν_2 and ν_3 vibrational frequencies in both the A′A′'' and a′A′'' states are smaller than the respective frequencies in the ground state because the NO bond length is elongated and the bond angle becomes larger in the excited states. This agrees with experimental values. For example, the vibrational frequencies in the ground state of HNO and HPO were calculated to be 2056 (ν_1), 995 (ν_2), and 1205 (ν_3) cm⁻¹, in comparison with the experimental values, 2095 (ν_1), 998 (ν_2), and 1188 (ν_3) cm⁻¹; respectively; the deviations from the experimental values are 39, 3, and 17 cm⁻¹, respectively. In the A′A′'' state, the calculated and experimental values have been reported as 566 and 858 cm⁻¹, respectively, and the present calculations yield the values as 635 and 878 cm⁻¹, respectively. No experimental data exist for the vibrational frequencies in the a′A′'' state; however, the present results are in agreement with those by the CASPT2 values.

### TABLE VI. Geometries and adiabatic excitation energy (eV) of the ground and excited states of HNO and HPO calculated by the direct SAC–CI SD–R method with cc-pVTZ–f basis sets.

<table>
<thead>
<tr>
<th>State</th>
<th>Method</th>
<th>r_HA (Å)</th>
<th>r_AO (Å)</th>
<th>θ (°)</th>
<th>T_0 (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X'A'</td>
<td>CASPT2</td>
<td>1.056</td>
<td>1.214</td>
<td>108.1</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>SAC–CI</td>
<td>1.051</td>
<td>1.210</td>
<td>107.9</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>Expt. (r_0,θ_0)</td>
<td>1.063(2)</td>
<td>1.212(1)</td>
<td>108.6(2)</td>
<td>...</td>
</tr>
<tr>
<td>A''</td>
<td>CASPT2</td>
<td>1.038</td>
<td>1.239</td>
<td>115.7</td>
<td>1.449</td>
</tr>
<tr>
<td></td>
<td>SAC–CI</td>
<td>1.034</td>
<td>1.241</td>
<td>114.6</td>
<td>1.646</td>
</tr>
<tr>
<td></td>
<td>Expt. (r_0,θ_0)</td>
<td>1.036(5)</td>
<td>1.241(1)</td>
<td>116.25(4)</td>
<td>1.631</td>
</tr>
<tr>
<td>a'A'</td>
<td>CASPT2</td>
<td>1.027</td>
<td>1.229</td>
<td>109.0</td>
<td>0.586</td>
</tr>
<tr>
<td></td>
<td>SAC–CI</td>
<td>1.023</td>
<td>1.229</td>
<td>118.1</td>
<td>0.707</td>
</tr>
<tr>
<td></td>
<td>Expt.</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>0.781</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HPO</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>X'A'</td>
<td>CASPT2</td>
<td>1.452</td>
<td>1.490</td>
<td>104.1</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>SAC–CI</td>
<td>1.460</td>
<td>1.493</td>
<td>104.3</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>Expt. (r_0,θ_0)</td>
<td>1.456(3)</td>
<td>1.480(5)</td>
<td>103.5(25)</td>
<td>...</td>
</tr>
<tr>
<td>A''</td>
<td>CASPT2</td>
<td>1.45</td>
<td>1.573</td>
<td>95.3</td>
<td>2.087</td>
</tr>
<tr>
<td></td>
<td>SAC–CI</td>
<td>1.451</td>
<td>1.585</td>
<td>93.3</td>
<td>2.346</td>
</tr>
<tr>
<td></td>
<td>Expt. (r_0,θ_0)</td>
<td>1.51(1)</td>
<td>1.549(3)</td>
<td>105(1)</td>
<td>2.360</td>
</tr>
<tr>
<td>a'A'</td>
<td>CASPT2</td>
<td>1.442</td>
<td>1.519</td>
<td>111.8</td>
<td>1.467</td>
</tr>
<tr>
<td></td>
<td>QCId</td>
<td>1.429</td>
<td>1.551</td>
<td>106.2</td>
<td>1.922</td>
</tr>
<tr>
<td></td>
<td>SAC–CI</td>
<td>1.428</td>
<td>1.530</td>
<td>110.3</td>
<td>1.646</td>
</tr>
</tbody>
</table>

*Reference 28.
*Reference 46.
*Reference 47.
*Reference 48.

The agreement with experiment is also reasonable for HPO. For example, the vibrational frequencies in the ground state were calculated to be 2095 (ν_1), 998 (ν_2), and 1188 (ν_3) cm⁻¹, in comparison with the experimental values, 2056 (ν_1), 995 (ν_2), and 1205 (ν_3) cm⁻¹, respectively; the deviations from the experimental values are 782 and 1426 cm⁻¹, respectively; and the present calculations yield the values as 755 and 1401 cm⁻¹, respectively.

The calculated vibrational frequencies of DNO and DPO within the BO approximation are summarized in Table VIII. Experimental values have been reported for the X'A', A''', and a'A'' states of DNO and for the X'A' and A''A'' states of DPO. The trend of the vibrational frequencies in the ground and excited states of DNO (DPO) and the deviations from the experimental values are almost parallel to those of HNO (HPO). The calculated values show fair agreement with the experimental values. For instance, the calculated ν_2 and ν_3 are 782 and 1426 cm⁻¹ (expt. 755 and 1401 cm⁻¹) for DNO and those for DPO are 478 and 867 cm⁻¹ (expt. 438(5) and 846(5) cm⁻¹).

The calculated vibrational energies of the lowest 20 vibrational levels and their assignments for HNO and HPO are summarized in the supplementary material of Table S4. The photoelectron spectra of HNO and DNO, the photoelectron spectra of HNO and DPO, and a detailed theoretical analysis will be reported in a separate note.

### E. Comparison with experimental values

To evaluate the performance of the SAC–CI SD–R nonvariational calculations with cc-pVTZ–f basis sets for the equilibrium geometries, adiabatic excitation energies, and vibrational frequencies, the theoretical and experimental values are compared in Figs. 6 and 7. Note that the experimental values
TABLE VII. Harmonic and anharmonic vibrational frequencies (cm$^{-1}$) of the ground and excited states of HNO and HPO calculated by the direct SAC–CI SD–R method with cc-pVTZ–f basis sets.

<table>
<thead>
<tr>
<th>State</th>
<th>Method</th>
<th>$\omega_1$ (HN/HP)</th>
<th>$\omega_2$ (bend)</th>
<th>$\omega_3$ (NO/PO)</th>
<th>$\nu_1$ (HN/HP)</th>
<th>$\nu_2$ (bend)</th>
<th>$\nu_3$ (NO/PO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1A'$</td>
<td>CASPT2$^a$</td>
<td>2778</td>
<td>1474</td>
<td>1526</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>SAC–CI</td>
<td>2991</td>
<td>1585</td>
<td>1630</td>
<td>2731</td>
<td>1543</td>
<td>1601</td>
</tr>
<tr>
<td></td>
<td>Expt. (gas)$^b$</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>2684</td>
<td>1501</td>
<td>1565</td>
</tr>
<tr>
<td></td>
<td>Expt. (Ar)$^b$</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>2716</td>
<td>1505</td>
<td>1563</td>
</tr>
<tr>
<td>$^1A''$</td>
<td>CASPT2$^a$</td>
<td>3184</td>
<td>975</td>
<td>1442</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>SAC–CI</td>
<td>3201</td>
<td>1033</td>
<td>1480</td>
<td>2946</td>
<td>1016</td>
<td>1444</td>
</tr>
<tr>
<td></td>
<td>Expt. (gas)$^b$</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>2854</td>
<td>982</td>
<td>1421</td>
</tr>
<tr>
<td></td>
<td>Expt. (Ar)$^b$</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>982</td>
<td>1422</td>
<td></td>
</tr>
<tr>
<td>$^3A''$</td>
<td>CASPT2$^a$</td>
<td>3471</td>
<td>1026</td>
<td>1530</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>SAC–CI</td>
<td>3380</td>
<td>1081</td>
<td>1571</td>
<td>3162</td>
<td>1051</td>
<td>1540</td>
</tr>
<tr>
<td></td>
<td>Expt. (gas)$^b$</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>992(150)</td>
<td>1402(140)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reference 28.
$^b$Fundamental frequencies taken from Ref. 42.

TABLE VIII. Vibrational frequencies of the ground and excited states of DNO and DPO calculated by the SAC–CI SD–R method with cc-pVTZ–f basis sets.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>State</th>
<th>Method</th>
<th>$\nu_1$(HA)</th>
<th>$\nu_2$(bend)</th>
<th>$\nu_3$(AX)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DNO</td>
<td>$^1X'A'$</td>
<td>SAC</td>
<td>2055</td>
<td>1182</td>
<td>1587</td>
</tr>
<tr>
<td></td>
<td>Expt. (Ar)$^a$</td>
<td>2043</td>
<td>1153</td>
<td>1547</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Expt. (gas)$^a$</td>
<td>2025</td>
<td>...</td>
<td>1546</td>
<td></td>
</tr>
<tr>
<td>$^1A''$</td>
<td>SAC–CI</td>
<td>2233</td>
<td>782</td>
<td>1426</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Expt. (gas)$^a$</td>
<td>2176</td>
<td>755</td>
<td>1401</td>
<td></td>
</tr>
<tr>
<td>$^3A''$</td>
<td>SAC–CI</td>
<td>2371</td>
<td>808</td>
<td>1525</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Expt. (gas)$^a$</td>
<td>...</td>
<td>750(140)</td>
<td>1452(140)</td>
<td></td>
</tr>
<tr>
<td>DPO</td>
<td>$^1X'A'$</td>
<td>SAC</td>
<td>1505</td>
<td>747</td>
<td>1203</td>
</tr>
<tr>
<td></td>
<td>Expt. (Ar)$^a$</td>
<td>1530</td>
<td>750</td>
<td>1186</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Expt. (gas)$^a$</td>
<td>...</td>
<td>745</td>
<td>1177</td>
<td></td>
</tr>
<tr>
<td>$^1A''$</td>
<td>SAC–CI</td>
<td>1443</td>
<td>478</td>
<td>867</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Expt. (gas)$^a$</td>
<td>...</td>
<td>438(5)</td>
<td>846(5)</td>
<td></td>
</tr>
<tr>
<td>$^3A''$</td>
<td>SAC–CI</td>
<td>1562</td>
<td>421</td>
<td>1019</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Fundamental frequencies taken from Ref. 42.

have uncertainty and some values were reported about three decades ago. The results of the bond lengths and bond angles for all of the molecules considered in the present work, that is, HCF, HCCI, HSIF, HSICl, HNO, and HPO, are compared with the experimental values in Fig. 6. The deviations from the line show the differences from the experimental values. Those of the vibrational frequencies and adiabatic excitation energies are shown in Fig. 7. In general, the agreement is excellent for HSiF (DSiF) and HSiCl (DSiF), whose experimental values were observed in recent works. Experimental errors might also exist, however, for the values of HNO (DNO) and HPO (DPO); a method with higher accuracy seems to be necessary.

The overall mean deviations from the experimental values are 0.015 Å for HA bond length, 0.018 Å for AO bond length, 0.6$^\circ$ for bond angle, and 0.069 eV for adiabatic excitation energy except for the apparently different values such as the bond angle of HPO in the $^1A''$ state. For the vibrational frequency, the mean deviation for HCF, HCCI, HSIF, and HSICl, and their isotopomers is 11.9 cm$^{-1}$ and that for HNO, HPO, and their isotopomers is 37.7 cm$^{-1}$.

IV. PERTURBATION SELECTION WITH LMOs

In the SAC–CI method, perturbation selection is effective for large-scale calculations on biological compounds and material-related molecules. The LMOs are effective for calculating the electron correlations and perturbation selection is effective with the use of LMOs. Various approaches of the local-correlation methods have been developed to calculate the electron correlations efficiently. However, in such cases, the PES may not be continuous and a singularity of the energy derivatives may appear. The MOD method has been developed for calculating the analytical energy gradients in a singularity-free manner. Therefore, perturbation selection based on the LMOs combined with the MOD method is expected to be a rigorous method for the analytical energy gradients of the SAC/SAC–CI method. We have applied this...
The present calculations of the equilibrium geometry and harmonic vibrational frequencies were performed in the following sequence:

1. The SAC–CI calculation was conducted with the LMOs and perturbation selection was performed. Pipek–Mezey population localization was used for calculating the LMOs.

2. During the geometry optimization, the MOD method was applied and the sets of excitation operators were fixed to those at the initial geometry. The “MacroIteration” was repeated until the forces and geometry parameters converged.

3. The harmonic vibrational frequencies were calculated from the second derivatives numerically computed with the analytical first derivatives. In this step, the MOD method was used with excitation operators being unchanged. For this purpose, the group sum option was used in the GAUSSIAN09 program. By using GSUM option, the excitation operators were fixed at the starting geometry and the summation of operators was not taken.

The initial structures of the geometry optimization were set to those obtained by the full calculations. In the present calculation, the “MacroIteration” was used and the dependence of the results on the initial geometry was small.

The results for the X1A′, A1A′′, and a3A′′ states of HSiF are summarized in Table IX with the deviations from the values obtained by the full calculations without perturbation selection. We have examined some thresholds in the perturbation selection; e.g., \( \lambda_g = 10^{-7}, 10^{-8}, \) and \( 10^{-9} \) for SAC and the corresponding thresholds, \( \lambda_e = 10^{-8}, 10^{-9}, \) and \( 10^{-10} \), respectively, for SAC–CI. The results with canonical MOs are also given in supplementary material of Table S5.45 The convergence of the results using LMOs is faster than those using canonical MOs considering the SAC/SAC-CI dimensions, in particular, for the vibrational frequency. The effect of LMOs, however, is not so prominent for small molecules. In the calculations with LMOs, the deviations in the A1A′′ state for example, are 3.12, 1.13, and 0.54 mhartree for \( \lambda_e = 10^{-8}, 10^{-9}, \) and \( 10^{-10} \), respectively. The errors in the transition energies from the full calculations are much small; for example, in the

<table>
<thead>
<tr>
<th>State</th>
<th>( \lambda_g, \lambda_e )</th>
<th>Dimension</th>
<th>( \Delta r_{HA} ) (Å)</th>
<th>( \Delta r_{AX} ) (Å)</th>
<th>( \Delta \theta ) (°)</th>
<th>( \Delta E ) (mhartree)</th>
<th>( \Delta \Delta E ) (eV)</th>
<th>( \Delta \omega_1 ) (SiF)</th>
<th>( \Delta \omega_2 ) (bend)</th>
<th>( \Delta \omega_3 ) (SiF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X1A′</td>
<td>( 10^{-7} )</td>
<td>10292</td>
<td>0.003</td>
<td>0.001</td>
<td>0.0</td>
<td>4.38</td>
<td>...</td>
<td>17</td>
<td>129</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>( 10^{-8} )</td>
<td>15355</td>
<td>0.000</td>
<td>0.000</td>
<td>0.0</td>
<td>1.26</td>
<td>...</td>
<td>11</td>
<td>48</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>( 10^{-9} )</td>
<td>18569</td>
<td>0.000</td>
<td>0.000</td>
<td>0.0</td>
<td>0.37</td>
<td>...</td>
<td>2</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>(40185)\textsuperscript{a}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>A1A′′</td>
<td>( 10^{-7}, 10^{-8} )</td>
<td>9592</td>
<td>0.003</td>
<td>0.001</td>
<td>0.4</td>
<td>3.12</td>
<td>0.034</td>
<td>16</td>
<td>47</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>( 10^{-8}, 10^{-9} )</td>
<td>13090</td>
<td>0.002</td>
<td>0.000</td>
<td>0.1</td>
<td>1.13</td>
<td>0.004</td>
<td>16</td>
<td>44</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>( 10^{-9}, 10^{-10} )</td>
<td>15668</td>
<td>0.000</td>
<td>0.000</td>
<td>0.0</td>
<td>0.54</td>
<td>0.005</td>
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<td>19</td>
<td>1</td>
</tr>
<tr>
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<td>(40185)\textsuperscript{a}</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a3A′′</td>
<td>( 10^{-7}, 10^{-8} )</td>
<td>11182</td>
<td>0.003</td>
<td>0.001</td>
<td>0.2</td>
<td>3.94</td>
<td>0.011</td>
<td>36</td>
<td>133</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>( 10^{-8}, 10^{-9} )</td>
<td>16491</td>
<td>0.001</td>
<td>0.000</td>
<td>0.1</td>
<td>1.39</td>
<td>0.004</td>
<td>13</td>
<td>61</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>( 10^{-9}, 10^{-10} )</td>
<td>20661</td>
<td>0.000</td>
<td>0.000</td>
<td>0.0</td>
<td>0.47</td>
<td>0.003</td>
<td>7</td>
<td>22</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(56118)\textsuperscript{a}</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( \textsuperscript{a} \) Dimension without perturbation selection.
\[ a^3 \text{Å}^n \] state, deviations are 0.011, 0.004, and 0.003 eV for \( \lambda_g = 10^{-5}, 10^{-9}, \text{and } 10^{-10}, \) respectively. The convergence of the geometrical parameters is very fast and a reliable structure with errors less than 0.003 Å can be obtained in the lowest level of calculations (\( \lambda_g = 10^{-7} \)). On the other hand, the convergence of the harmonic vibrational frequencies is relatively slow, in particular for the bending mode, which is a soft coordinate. However, it is much faster than the calculations with canonical MOs. The convergence of the harmonic frequencies in the symmetric (\( \omega_1, \text{HSi} \)) and antisymmetric (\( \omega_2, \text{SiF} \)) modes is relatively fast.

The results for some other molecules in the present study also show similar trends. The present method, the perturbation-selection scheme using LMOs, is useful for geometry optimization to calculate the ground- and excited-state equilibrium geometries; however, it should be carefully used for calculations of the harmonic vibrational frequencies at the equilibrium geometries.

V. SUMMARY

In this work, the analytical energy gradients of the direct SAC–CI SD–R nonvariational method have been applied to calculate the excited-state equilibrium geometries and vibrational frequencies of the valence excited states of bent HAX-type molecules. For calculating the harmonic vibrational frequencies, the second derivatives have been computed numerically using the analytical first derivatives. The 3D PESs around the local minima were used to evaluate the anharmonicity of the vibrational frequencies.

The calculations have been performed for the lowest singlet and triplet states (\( \text{\(^3\)}A', \text{\(^2\)}A') of HCX (\( X = F, Cl \)), HSiX (\( X = F, Cl \)), and HAO (\( A = N, P \)), some of which have been well studied by high-resolution spectroscopy and \textit{ab initio} calculations. The vibrational analysis has also been performed for these molecules and their isomers, DCX (\( X = F, Cl \)), DSiX (\( X = F, Cl \)), and DAO (\( A = N, P \)). The calculated results show good agreement with the available experimental values and other theoretical values, which show the reliability of the method. The vibrational level emission spectra of HSIF and DSIF and absorption spectra of HSICl and DSICl were simulated within the FC approximation. The peak positions and relative intensities of the vibrational peaks were well reproduced, which show the well-balanced description of the ground and excited states by the SAC/SAC–CI method. The geometry changes in the excited states are interpreted based on the electrostatic theory using the electron density difference between the ground and excited states.

Geometry optimization using perturbation selection combined with the MOD method and LMOs is shown to be effective for calculating the excited-state geometry. However, it should be carefully used for calculating the harmonic vibrational frequencies, in particular for soft modes such as bending and torsion coordinates.

ACKNOWLEDGMENTS

This study was supported by JST-CREST, a Grant-in-Aid for Scientific Research from the Japanese Society for the Promotion of Science (JSPS) and the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan and the Next Generation Supercomputing Project. The computations were partly performed using the Research Center for Computational Science in Okazaki, Japan.

See supplementary material at http://dx.doi.org/10.1063/1.3617233 for the vibrational levels of HCF, DCF, HCCl, DCCl, HSiCl, DSiCl, HPO, and DPO calculated by the SAC-CI 3D PESs. The examination of perturbation selection with canonical MOs is also given.
M. Ebara, T. Miyahara, and H. Nakatsuji, “Photodetachment spectra of HNO and DNO anions studied by the analytical energy gradients of SAC-CI method” (unpublished).