First-principles study on the energetics and vibrational properties of the S2 - impurity in alkali-halide crystals

First-principles study on the energetics and vibrational properties of the S$_2^-$ impurity in alkali-halide crystals

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We have performed first-principles electronic structure calculations for the S$_2$ and S$_2^-$ molecules in the vacuum and found that the calculated equilibrium bond lengths and vibrational spectroscopic constants are in good agreement with the experiments as well as the previous calculations. Based on this conformation we extended these calculations to the substitutional S$_2^-$ molecule in the alkali halides, such as NaCl, NaBr, NaI, KCl, KBr, KI, RbCl, RbBr, and RbI. It is found from these calculations that the S$_2^-$ center aligned to [110] direction is generally favorable over those with the [100] and [111] orientations, in agreement with the experiments. We also found that the vibrational frequencies of the S$_2^-$ anion in the alkali halides shift to higher energies with decreasing lattice parameters. These results suggest that the change in the bond length of the S$_2^-$ anion in the matrices depends on the species of halogen atom, while the frequencies are influenced by the species of alkali atom.

I. INTRODUCTION

When alkali halides are annealed under chalcogen (Ch) vapors such as oxygen, sulfur, and selenium gases, Ch impurity molecules are easily dissolved in alkali halides. The vibrational and electronic properties of Ch impurity molecule in alkali halides have been extensively investigated experimentally using optical spectra,[1–8] electron paramagnetic resonance (EPR),[9,10] and electron-nuclear double resonance (ENDOR).[11] These experiments revealed that the substitutional S$_2^-$ molecular ions are generally formed at halogen ion sites. The orientation of the molecule in the ground state is [110], while the unpaired paramagnetic *p* lobes are pointing to either [$\bar{1}$10] or [001] depending on the host matrices. In contrast to these extensive experimental studies, theoretical investigations have been limited to empirical calculations[12] and unified understanding of the spectroscopic feature of the S$_2^-$ impurity in the host matrices environments has not yet been achieved.

Accurate and systematic study of the local vibrational mode of sulfur molecule in various alkali halides is a computational challenge of first-principles theory as it requires detailed structural and electronic information of the bonding nature. In addition, it may stimulate close interplay between theory and experiments in this research field. The purpose of the present work is to investigate the energetics and vibrational properties of the S$_2^-$ molecule in the various alkali halide matrices (NaCl, NaBr, NaI, KCl, KBr, KI, RbCl, RbBr, and RbI) based on the density-functional electronic structure calculation using a large supercell approximation.

II. CALCULATIONS FOR PURE SYSTEMS

A. Pure alkali halides

The calculations were performed using the first-principles simulation code VASP.[13–16] In these calculations the projector augmented-wave (PAW) method[17,18] and the generalized gradient approximation (GGA) were used to evaluate the total energies and the Perdew-Wang exchange-correlation functional (PW91) (Ref. 19) was employed in the GGA. The reciprocal space integrations were performed using the 6^3 Monkhorst-Pack (MP) mesh.[20] The atomic coordinates were relaxed using a conjugate gradient algorithm with the tolerance of 0.01 eV/Å for the maximal atomic force.

We first evaluated the equilibrium lattice parameters of the alkali halides as a test of the PAW-PW91 method and for later use in the study of S$_2^-$ center in the alkali halides. Well-converged results were obtained by using the cutoff energies in the plane-wave basis expansion of 300 eV for NaCl, NaBr, and NaI, 262.44 eV for KCl and RbCl, 216.26 eV for KBr and RbBr, and 175.64 eV for KI and RbI. The calculated and experimental[21] lattice parameters are summarized in Table I. The lattice parameters obtained by the self-consistent atomic deformation (SCAD) method[22] with the use of the local-density approximation[23] (LDA) for the exchange-correlation functional are also shown for comparison. We find that the lattice parameters calculated by the SCAD-LDA are generally underestimated, while the PAW-PW91 yields the opposite but better results except for NaBr. In the following, we use the PAW-PW91 optimized lattice parameters for consistency.

TABLE I. Calculated and experimental lattice parameters of alkali halides in unit of angstrom. The values in the parentheses are the deviations from the experiments (Expt.).

	NaCl	NaBr	NaI	KCl	KBr	KI	RbCl	RbBr	RbI
Expt. (Ref. 21)	5.64	5.97	6.47	6.29	6.60	7.07	6.58	6.85	7.34
PAW-PW91 (Present)	5.68	6.05	6.53	6.31	6.64	7.15	6.61	6.95	7.46
	(0.04)	(0.08)	(0.06)	(0.02)	(0.04)	(0.08)	(0.03)	(0.10)	(0.12)
SCAD-LDA (Ref. 22)	5.58	5.96	6.40	6.08	6.37	6.77	6.39	6.65	7.04
	(-0.06)	(-0.01)	(-0.07)	(-0.21)	(-0.23)	(-0.30)	(-0.19)	(-0.20)	(-0.30)

B. Sulfur molecule in the vacuum

We next evaluated the equilibrium bond length of sulfur molecule in the vacuum using the PAW-PW91. Only the Γ point is considered in the reciprocal space integration and the cutoff energy of 260 eV is used in the plane-wave basis expansion. Initially, a diatomic sulfur molecule with optional bond length is put in the large cubic supercell with the volume of 10^3 Å^3. The electronic ground states of sulfur molecules S_2 and S_2^- in the vacuum are represented by the $^3\Sigma_g^-$ and $^2\Pi_g$, respectively. We add one extra electron to the S_2 molecule to investigate $^2\Pi_g$ electronic state of the S_2^- anion, while a ferromagnetic spin configuration of the S_2 molecule represents the $^3\Sigma_g^-$ electronic state. After the structural relaxations, we obtained equilibrium bond lengths r_e of the S_2 and S_2^- molecules as shown in Table II. The bond lengths calculated by the multireference configuration interaction (MRCI) method[24] and the Gaussian-orbital cluster (GOC) method[25] in the LDA and the GGA exchange-correlation functionals of PW91 and of Perdew, Burke, and Ernzerhof (PBE) (Ref. 26) are also shown for comparison. The present

results (PAW-PW91) show good agreement with the MRCI and GOC results as well as with the experimental ones,[27,28] indicating that our calculations are reliable enough to be used in later analyses of the S_2^- molecules in the alkali halides.

We also estimated the harmonic and anharmonic spectroscopic constants ω_e and $\omega_e x_e$ of the S_2 and S_2^- molecules by a simple perturbation theory for the one-dimensional anharmonic oscillator. In these calculations we assumed that the potential energy of a diatomic molecule about the equilibrium bond length of $r=r_e$ can be expressed as

$$E(r)=E(r_e)+\frac{k}{2}(r-r_e)^2+\alpha(r-r_e)^3+\beta(r-r_e)^4. \quad (1)$$

The harmonic force constant k of the quadratic term yields the harmonic frequency $\omega_e=\sqrt{k/M}$, where M denotes the reduced mass, and the anharmonic correction $\Delta\omega=-2\omega_e x_e$ due to the cubic and quartic terms is given by[29,30]

$$\Delta\omega=3\frac{\hbar}{M}\left[-\frac{5}{2}\left(\frac{\alpha}{k}\right)^2+\frac{\beta}{k}\right]. \quad (2)$$

TABLE II. Present results for the equilibrium bond lengths r_e and the spectroscopic constants ω_e and $\omega_e x_e$ of the S_2 and S_2^- molecules in their ground states and their comparisons with the previous calculations and experiments.

	S_2 ($^3\Sigma_g^-$)	S_2^- ($^2\Pi_g$)
r_e (Å)		
PAW-PW91 (Present)	1.909	2.022
MRCI (Ref.24)	1.908	2.019
GOC (LDA, PW91, PBE) (Ref. 25)	(1.900, 1.918, 1.916)	
Expt. (Refs. 27 and 28)	1.889	2.005 ± 0.015
ω_e (cm^{-1})		
PAW-PW91 (Present)	699.50	552.95
MRCI (Ref. 24)	734	582
GOC (LDA, PW91, PBE) (Ref. 25)	(700, 700, 695)[a]	–
Expt. (Refs. 27 and 28)	725	600.8[b]
		570 ± 100[c]
$\omega_e x_e$ (cm^{-1})		
PAW-PW91 (Present)	3.34	1.29
Expt. (Ref. 27)	2.84	3.01

[a]Frequency of S_2 molecule including anharmonic correction calculated by GOC with the GGA (PBE) exchange-correlation functional is reported as 684 cm^{-1} (Ref. 25).
[b]Frequency of S_2^- molecule dissolved in KI. Gaseous phase frequency has been predicted as $\sim$550 cm^{-1} (Ref. 27).
[c]Frequency of S_2^- molecule deduced from the vibrational progression (Ref. 28).

TABLE III. Calculated and experimental equilibrium bond lengths r_e (in unit of angstrom) of halogen molecules in the vacuum and their comparisons with the experiments. The results for chlorine molecule obtained by the GOC method in the LDA and GGA (PW91 and PBE) are also shown in the parentheses.

	Cl_2	Br_2	I_2
PAW-PW91 (Present)	2.009	2.309	2.687
GOC (LDA, PW91, PBE) (Ref. 25)	(1.994, 2.022, 2.020)		
Expt. (Ref. 27)	1.988	2.281	2.666

We performed a series of calculations to estimate the potential energy $E(r)$ for the stretching mode of sulfur molecule in the vacuum. The total energy of the supercell was calculated for more than eight bond lengths in the range of $|r - r_e| \leq 0.5$ Å about the equilibrium. The calculated total energies were fitted to Eq. (1) using the least-squares method to obtain the force constants k, α, and β. The harmonic and anharmonic frequencies of the molecules in the vacuum obtained in this way are also given in Table II. The calculated harmonic force constants are 14.42 eV/Å^2 and 9.01 eV/Å^2 for S_2 and S_2^- molecules, respectively. The isotope shifts of the frequencies are not included in Table II since the evaluation is straightforward. We find that the harmonic frequencies ω_e obtained in our calculations are underestimated as compared to the experimental values. The same tendency of underestimation has also been observed in the LDA calculations of light molecule H_2 in the gaseous phase as well as the H_2 impurity at the tetrahedral interstitial site of Si and GaAs semiconductors.[30] We note that the harmonic frequencies of both S_2 and S_2^- molecules calculated by MRCI method are larger than the present results by 30 cm^{-1}. The calculated harmonic frequencies $\omega_e \simeq 700$ cm^{-1} of S_2 molecule by the GOC method in the LDA and GGA (PW91 and PBE) are in good agreement with ours. While the experimental harmonic frequency 600.8 cm^{-1} was obtained for the S_2^- molecule dissolved in KI,[1–3] the gaseous phase frequency[27] of the S_2^- anion has been predicted as ~ 550 cm^{-1} and consistent with our estimated value of 552.95 cm^{-1}. However, this agreement is marginal because of the large experimental error[28] of 570 ± 100 cm^{-1}.

C. Halogen molecules in the vacuum

The equilibrium bond lengths and the total energies of the halogen molecules in the vacuum were also calculated. The computational method was the same as that for sulfur molecule and we used the cutoff energies of 262 eV, 216 eV, and 175 eV in the plane-wave basis expansion for Cl_2, Br_2, and I_2 molecules, respectively. After structural relaxations, we obtained the equilibrium bond lengths r_e of the halogen molecules as given in Table III. These results show good agreement with the experiments.[27] The previous results for chlorine molecule obtained by the GOC (Ref. 25) in the LDA and GGA (PW91 and PBE) are also shown for comparison. Although the same exchange-correlation functional of PW91 was employed, the present and the GOC-PW91 calculations yield slightly different equilibrium bond lengths of the chlorine molecule. This is probably due to the difference in the

computational details such as the types of basis set. The bond length obtained by the GOC method in the GGA (PBE) exchange-correlation functional (GOC-PBE) is also slightly overestimated as compared to the experimental results. These overestimations are typical in the GGA calculations as actually found in the case of sulfur molecule.

III. S_2^- CENTER IN THE ALKALI HALIDES

We now proceed to the study on the energetics and vibrational properties of the S_2^- center in the alkali halides. By heating the alkali halide crystals in the presence of sulfur gas, sulfur molecules are easily dissolved into the alkali halides and form the S_2^- molecular impurity centers at halogen ion sites. The orientation of the molecule in the ground state is [110] while the paramagnetic p lobes are pointing to either $[\bar{1}10]$ or [001] depending on the host matrices, as actually observed for NaCl,[10,31] NaBr,[32,33] NaI,[9,33] KCl,[9,31] KBr,[2,9] KI,[1–3] RbCl,[34,35] RbBr,[2,9,34] and RbI (Refs. 2, 9, and 11) by the EPR and ENDOR methods. The optical emission spectra of the S_2^- center in NaI,[2,6] KCl,[2] KBr,[2] KI,[1–5] RbCl,[6] RbBr,[2] and RbI (Refs. 2 and 4) crystals have also been extensively studied. In the following, we show the results of our studies on the S_2^- centers dissolved in these alkali halides including NaCl and NaBr. Although there has been no report, to the best of our knowledge, on the experimental spectroscopic data for the S_2^- molecule in NaCl and NaBr crystals, progress in the optical experiment will enable us to probe such vibrational properties of the molecule.

The formation energy of the S_2^- center at halogen ion site is given by

$$E_f^{[xyz]} = E_{total}^{S_2^-[xyz]} - E_{total} + \mu_{halogen} - \mu_{S_2}. \quad (3)$$

Here, E_{total} is the total energy of the pure alkali halide supercell composed of 32 unit cells (64 atoms in total) and is equal to 32 times of μ_{ah}, the calculated total energy per unit cell of the alkali halide in its optimized lattice constant ($E_{total} = 32\mu_{ah}$), $E_{total}^{S_2^-[xyz]}$, is the total energy of the defect supercell having a S_2^- center with the orientation of $[xyz]$, $\mu_{halogen}$ is the atomic chemical potential of halogen atom and is equal to half of the total energy of a free diatomic halogen molecule in the vacuum, and μ_{S_2} the chemical potential of S_2 molecule and is equal to the total energy of a free diatomic sulfur molecule in the vacuum. The formation energy calculated in this manner corresponds to the energy cost to form S_2^- center in the alkali halide in the limit of the

TABLE IV. Relative formation energy $\Delta E_f^{[xyz]}$ and its averaged standard value $\langle E_f \rangle_{av}$ of the S_2^- center (in unit of eV). The underlines indicate the orientations of the molecular center with the lowest formation energy.

Matrices	$\Delta E_f^{[100]}$	$\Delta E_f^{[110]}$	$\Delta E_f^{[111]}$	$\langle E_f \rangle_{av}$
NaCl	0.662	-0.405	-0.257	2.889
NaBr	0.555	-0.334	-0.222	1.559
NaI	0.729	-0.459	-0.269	-0.291
KCl	0.261	-0.135	-0.125	2.693
KBr	0.242	-0.137	-0.106	1.804
KI	0.208	-0.106	-0.101	0.493
RbCl	0.186	-0.118	-0.067	3.649
RbBr	0.156	-0.078	-0.078	2.738
RbI	0.184	-0.055	-0.128	1.604

halogen gas rich condition. All the quantities except for $E_{total}^{S_2^-[xyz]}$ are easily obtained from the results in the preceding section. The calculations of $E_{total}^{S_2^-[xyz]}$ were performed by essentially the same method employed for the pure alkali halides and the computational details are as follows. Initially, a halogen atom in the supercell of an alkali halide is simply replaced by a sulfur molecule S_2 aligned to the $[xyz]$ direction. The substitute center attracts an electron released from the neighboring alkali atoms and its electronic state spontaneously changes to $^2\Pi_g$ (S_2^-). Then, all the atomic positions including those of S_2^- are fully relaxed and optimized under the constraint that the lattice parameter is fixed to that of the pure alkali halides (Table I). We adopted the cutoff energy larger than 260 eV and the 2^3 MP mesh reciprocal space integrations in all the calculations of the defect supercell systems to retain the accuracy in the presence of sulfur center.

It is convenient to use the relative formation energy $\Delta E_f^{[xyz]}$ of the S_2^- center with the $[xyz]$ orientation in the alkali halide crystals, which is defined as

$$\Delta E_f^{[xyz]} = E_f^{[xyz]} - \langle E_f \rangle_{av}, \tag{4}$$

with

$$\langle E_f \rangle_{av} = (E_f^{[100]} + E_f^{[110]} + E_f^{[111]})/3. \tag{5}$$

We use the standard procedure to calculate the defect formation energy given by Eq. (3).[36] The chemical potential of an alkali halide (the calculated total energy per unit cell of the alkali halide) is constrained by the relation

$$\mu_{ah} = \mu_{alkali} + \mu_{halogen}, \tag{6}$$

where μ_{alkali} is the chemical potential of the alkali atom. In the limit of alkali metal rich condition μ_{alkali} is given by the total energy per atom of the pure metallic phase. The value of $\mu_{halogen}$ determined by using that value of μ_{alkali} in the above constraint relation is reduced by the enthalpy of formation of the alkali halide compared to that determined in the halogen gas rich limit and this leads to the energy shift of $\langle E_f \rangle_{av}$ by the same amount. We refer to the formation energy at halogen gas rich limit in the following although such an

TABLE V. Calculated equilibrium bond lengths and the spectroscopic constants of S_2^- molecule with [110] orientation in the alkalihalide matrices. The values for * ord and * extra are the experimental results, where "ord" and "extra" stand for *ordinary* and *extra* vibrational frequencies, respectively, in the emission spectra.

Matrices	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})
Vacuum [a]	2.022	552.95	1.29
NaCl	2.000	614.20	2.59
NaBr	2.005	570.79	3.13
NaI	2.025	560.72	2.36
* ord [b]		587±1	3.7±0.1
KCl	1.987	610.64	2.24
* ord [b]		623.1±0.3	2.26±0.04
* extra [b]		627.4±0.3	2.44±0.02
KBr	2.000	596.31	1.99
* ord [b]		614.3±0.2	2.53±0.01
* extra [b]		614.1±0.4	2.48±0.03
KI	2.014	593.38	2.17
* ord [c]	1.98	600.8	2.53
* ord [b]		597.8±0.2	3.01±0.03
* extra [b]		598.6±0.2	2.16±0.03
RbCl	1.988	607.73	2.20
RbBr	2.000	591.87	2.29
* extra [b]		614.5±0.2	2.49±0.01
RbI	2.012	570.63	2.44
* ord [b]		599.4±0.1	2.53±0.01
* extra [b]		603.1±0.3	2.54±0.02

[a]Quoted from Table II.
[b]Reference 2.
[c]Reference 1.

energy shift is irrelevant in the relative value given by Eq. (4). We also note that the influence of absolute numerical error can be restrained by using $\Delta E_f^{[xyz]}$ rather than $E_f^{[xyz]}$ itself in the examination of the relative stability. The calculated results of $\Delta E_f^{[xyz]}$ and $\langle E_f \rangle_{av}$ for the S_2^- center in alkali halides are summarized in Table IV. We find that the orientation [110] is generally favorable over the [100] and [111] orientations in the ground state, which is consistent in most cases with the experimental findings of the universal orientation of [110] in the alkali halides. We note that the calculated formation energies of the S_2^- molecule aligned to [110] and [111] are the same in RbBr, and the relative stability is turned over in RbI. The discrepancy between theory and experiments for RbBr and RbI may be ascribed to the underestimation of the compressive crystal field due to slight overestimations of the lattice parameter. The difference between $\Delta E_f^{[100]}$ and $\Delta E_f^{[110]}$ decreases in order of sodium halides, potassium halides, and rubidium halides. This trend roughly follows the order of increasing lattice constants and can be understood from the geometrical point of view, i.e., the room left for the molecule with the orientation [100] is proportional to the lattice constant itself in the rigid-ion picture. It should be noted that $\Delta E_f^{[100]}$ of KCl is much lower than that of NaI despite smaller lattice constant of KCl compared with that of NaI.

We next calculated the spectroscopic constants of S_2^- in the alkali halides. The host-matrices were *frozen* at their fully relaxed atomic configurations and only the sulfur molecule of [110] orientation was stretched along the orientation about its equilibrium bond length r_e to calculate the vibrational frequencies of S_2^- in the alkali halides. The results obtained in this way are summarized in Table V. Here the terms of *ordinary* and *extra* were introduced by Ikezawa and Rolfe to identify the different series of vibrational frequencies in the emission spectra. The origin of multiple series in the experimentally observed emission and absorption spectra of Ch_2^- molecule with [110] orientation in alkali halides has been thought to be the D_{2h} crystal-field splitting;[6] each vibrational level in the $^2\Pi_g$ ground state ($^2\Pi_u$ excited state) splits into two levels $^2B_{2g}$ and $^2B_{3g}$ ($^2B_{2u}$ and $^2B_{3u}$). In the emission spectra corresponding to the $^2\Pi_u \rightarrow ^2\Pi_g$ transition, the splitting of *ordinary* and *extra* vibrational frequencies is caused by the $^2B_{2g}$ and $^2B_{3g}$ splitting of the $^2\Pi_g$ ground state. The sharp zero-phonon emission peaks corresponding to $^2B_{3u} \rightarrow ^2B_{2g}$ transition have been called *ordinary* spectra and are comparable to our calculated equilibrium frequencies ω_e. However, it is difficult to identify very weak multiple splitting of the $^2\Pi_g$ ground state by the current computational approach. Hence we show the *ordinary* and *extra* frequencies of emission spectra in Table V for complementing the computational limitations. While the numerical precision of $\delta\epsilon = 0.01$ eV corresponding to 86.55 cm^{-1} is still much poorer than the required tolerance for the frequencies ω_e studied here, the relative accuracy may be retained well below that limit as indicated by the good agreements between the calculated and experimental frequencies (Table V). The deviation of the calculated frequencies from the experimental values is quite systematic (being underestimation of only 10–30 cm^{-1}), indicating high accuracy of the present calculations.

The harmonic frequencies ω_e shift to higher energies with decreasing lattice parameters because of the compressive crystal-field effects of the alkali-halide matrices. The calculated anharmonic contributions $\omega_e x_e$ of the S_2^- anion are in the range from 2 cm^{-1} to 3 cm^{-1}. These values reflect the enhanced anharmonicity of the potential energies in the alkali halides and somewhat larger than that of the S_2^- anion in the vacuum ($\omega_e x_e = 1.29$ cm^{-1}). Although there has been no optical experiment on the S_2^- center dissolved in NaCl and NaBr, the harmonic frequencies are expected to be 614 $+20$ cm^{-1} and $570+20$ cm^{-1} for NaCl and NaBr, respectively. Here we have taken into account the typical underestimation by 20 cm^{-1} of the calculated frequencies. The predicted equilibrium bond lengths of the S_2^- anion in the alkali halides are not much different from that in the vacuum ($r_e = 2.022$ Å). Furthermore, the trends in the variations of equilibrium bond lengths of the S_2^- anion in the potassium halides and the rubidium halides are similar. From this simi-

larity we may conclude that the change in the bond length of the S_2^- anion depends on the species of halogen atom rather than the species of alkali atom. Since one S_2^- anion impurity substitutes one halogen atom, the room for the S_2^- anion is equal to the ionic radius of the substituted halogen atom and its magnitude has an influence on the equilibrium bond length in the rigid-ion picture. While the same equilibrium bond length of $r_e = 2.000$ Å is predicted for the S_2^- anion in some of alkali halide host matrices (NaCl, KBr, and RbBr), the calculated harmonic frequencies ω_e decrease in order of NaCl, KBr, and RbBr. These results suggest that the frequency of the S_2^- anion is determined primarily by the species of surrounding alkali atoms through the modification of the potential-energy shapes while keeping its energy minimum at $r_e = 2.000$ Å. The modification of potential energy shapes is caused by the ionic radius and ionicity levels of neighboring alkali atoms. Detailed analysis of the electron orbitals of the S_2^- anion in various alkali halide matrices would be useful to check this interpretation.

IV. CONCLUSIONS

We have studied the energetics and vibrational properties of the S_2^- anions dissolved in a series of alkali halides. We first evaluated the equilibrium lattice parameters of the pure alkali halides using the PAW-PW91 method and obtained good agreement with experiments. The calculated spectroscopic constants and equilibrium bond lengths of the S_2 molecule and S_2^- anion in the vacuum also show good agreements with the experiments. Based on these reliable results we have calculated the relative formation energies of the S_2^- center with the orientations of [100], [110], and [111] in the alkali halides and found that the [110] orientation is generally favorable over the other orientations in the ground states. The harmonic frequencies of the S_2^- anion in the alkali halides obtained in the present study shift to higher energies with decreasing lattice parameters because of the compressive crystal field of the alkali halide matrices. Our results also suggest that the change in the bond length of the S_2^- anion in alkali halide matrices depends on the species of halogen atom, while the frequencies are primarily influenced by the species of alkali atom. We expect that these findings are fully supported by more detailed experimental studies in future.

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