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**Supporting Information**

**ABSTRACT:** Despite its relevance, the microscopic origin of the energy barrier, $B$, between the compressed and elongated geometries of Jahn–Teller (JT) systems is not well understood yet because of a lack of quantitative data about its various contributions. Seeking to clear up this matter, we have carried out both periodic and cluster ab initio calculations on the model system NaCl:Ni. This system is particularly puzzling because, according to experimental data, its barrier is much smaller than that for other d$^7$ and d$^9$ ions in similar lattices. All calculations performed on the model system lead, in fact, to values of $B \leq 160$ cm$^{-1}$, which are certainly smaller than $B = 500$ cm$^{-1}$ derived for NaCl:M$^{2+}$ (M = Ag, Rh) or $B = 1024$ cm$^{-1}$ obtained for KCl:Ag$^{2+}$. As a salient feature, analysis of calculations carried out as a function of the $Q_0$ ($\sim 3x^2 − y^2$) coordinate unveils the microscopic origin of the barrier. It is quantitatively proven that the elongated geometry observed for NaCl:Ni$^{2+}$ is due to the 3d–4s vibronic admixture, which is slightly larger than the anharmonicity in the eg JT mode that favors a compressed geometry. The existence of these two competing mechanisms explains the low value of $B$ for the model system, contrary to cases where the complex formed by d$^7$ or d$^9$ ions is elastically decoupled from the host lattice. Although the magnitude of $B$ for NaCl:Ni$^{2+}$ is particularly small, the tunneling splitting, 3|$\Gamma$, is estimated to be below 9 cm$^{-1}$, thus explaining why the coherence is easily destroyed by random strains and thus a static JT effect is observed experimentally. As a main conclusion, the barrier in JT systems cannot be understood neglecting the tiny changes of the electronic density involved in small distortions. The present calculations reasonably explain the experimental g tensor of NaCl:Ni$^{2+}$, pointing out that the d–d transitions in NiCl$_6^{2−}$ are much smaller than those for CuCl$_6^{4−}$ and the optical electronegativity of Ni$^{2+}$ is only around 1.

**1. INTRODUCTION**

A fundamental question to be answered in the research of materials is the actual origin of their structure and its relationship with the arrangement of electronic levels. To gain better insight into this relevant matter is certainly not easy because compounds that are similar in composition do not always display the same structure. For instance, at low temperatures, KMgF$_3$ and KNiF$_3$ perovskites are both cubic, while KMF$_3$ is tetragonal. In the same vein, there is a striking difference in the geometry of the CuCl$_4$(NH$_3$)$_2^{2−}$ and CuCl$_4$(H$_2$O)$_2^{2−}$ centers formed, for example, in Cu$^{2+}$-doped NH$_4$Cl. While the first center is tetragonal with four equivalent Cl$^{−}$ ligands, the substitution of axial NH$_3$ molecules by another neutral molecule, H$_2$O, produces a big orthorhombic distortion in the equatorial plane. Despite these facts, to understand what among two or more possible phases of a compound becomes the most stable at low temperatures is not a simple question because energy differences on the order of 100 cm$^{-1}$ or below are often involved.

A situation of this kind is found in the realm of the $E_g$⊗$e_g$ Jahn–Teller (JT) effect widely studied in the case of d$^7$ and d$^9$ ions in cubic insulating lattices under octahedral coordination. In these cases, the dependence of the ground-state energy as a function of $Q_0$ ($\sim 3x^2 − r^2$) and $Q_1$ ($\sim x^2 − y^2$) coordinates exhibits three equivalent adiabatic minima, involving tetragonal distortions along the three main axes, which are separated by an energy barrier $B$ (Figure 1). This barrier plays a key role for understanding the properties of JT systems. In fact, the existence of a low barrier is a necessary condition for observing coherent tunneling among the different minima in electron paramagnetic resonance (EPR) experiments, a phenomenon termed the dynamic JT effect. By contrast, as often happens, the unavoidable random strains, present in any real crystal, destroy the coherence, giving rise to the static JT effect. In this case, the sign of $B$ determines...
whether the equilibrium geometry corresponds to an elongated or a compressed octahedron and thus the electronic ground state. So, if in the warped surface depicted in Figure 1, the minima describe an elongated conformation and the saddle points correspond to a compressed one, $B > 0$, while the reverse happens if $B < 0$. Accordingly, if $B > 0$, the electronic ground state is $B_{1g}$ for a $d^9$ ion and $A_{1g}$ for a $d^7$ ion. Furthermore, in a static JT effect, the barrier controls the rate of incoherent transitions among the three wells and thus the passage of a tetragonal EPR spectrum to an isotropic one when the temperature is raised.\(^9,10,12\)

Despite its relevance, little is still known on the actual values of $B$ for JT systems and the microscopic origin of the energy barrier. This work is devoted to improve our quantitative knowledge on this matter by exploring in some detail the origin of $B$ for the model system NaCl:Ni\(^{+}\).\(^{15}\) This system has been chosen for the following reasons: (i) The low value of $T_1 = 35$ K, at which the static EPR spectrum\(^15\) of NaCl:Ni\(^{+}\) in the X band starts to disappear suggests that its barrier, $B$, is clearly smaller than that for other $d^9$ ($\text{Ag}^{2+}, \text{Cu}^{2+}$)\(^{16,17}\) and $d^7$ ($\text{Rh}^{2+}$)\(^{18}\) ions in the same host lattice, a surprising fact that deserves to be explored. (ii) Despite the small $B$ value expected for NaCl:Ni\(^{+}\), the low-temperature EPR spectra clearly prove that the JT effect is static and not dynamic.\(^15\) (iii) It has been shown\(^11\) that the vibronic 4d$\rightarrow$5s admixture for NaCl:Rh\(^{2+}\) makes an important, though not dominant, contribution to $B$. As the nd$\rightarrow$(n+1)s admixture on $B$ are expected to be enhanced in a system like NaCl:Ni\(^{+}\).

It was earlier argued by Opik and Pryce\(^20\) that the barrier in a JT system is due to the anharmonicity present in the $e_g$ vibration mode. Accordingly, a $\text{MX}_6$ complex ($M = d^9$ or $d^7$ ion) embedded in an insulating cubic lattice would prefer an elongated over a compressed geometry provided it is elastically decoupled from the rest of the lattice where it is embedded.\(^11,21\) By contrast, other authors\(^12,22,23\) have ascribed the origin of $B$ to the quadratic JT term involving operators that depend quadratically on $Q_0$ and $Q_z$ coordinates. However, a previous quantitative study performed on several JT systems points out that the quadratic JT term plays a minor role while the vibronic admixture of $e_g$ orbitals ($\sim 3z^2 - r^2; \sim x^2 - y^2$) with other ones due to the linear JT term but treated in second-order perturbations yields an important contribution\(^11\) to $B$. More precisely, in NaCl:Rh\(^{2+}\), about 40% of the barrier has been shown to come from the vibronic admixture of the $a_{2g}^x(\sim 3z^2 - r^2)$ orbital with the mainly 5s level of Rh\(^{2+}\), although the dominant contribution does arise from the anharmonicity.\(^11\) Moreover, because the RhCl\(_6^4^-\) complex in NaCl is elastically decoupled from the rest of the lattice, both contributions have been shown\(^11,13,14\) to favor an elongated geometry, making $B = 511$ cm$^{-1}$. These results explain our interest in Ni\(^{+}\) systems because the 3d$\rightarrow$4s separation is only 2 eV for the free ion while values close to 10 eV correspond to the 4d$\rightarrow$5s separation for free Ag\(^{2+}\) or Rh\(^{2+}\) ions.\(^19\) The influence of the 3d$\rightarrow$4s mixing on the equilibrium geometry of Cu\(^{2+}\) complexes has previously been suggested by several authors.\(^24-28\)

Although Ni\(^{+}\) is an unusual oxidation state for nickel, such a valence has been stabilized in lattices like $\text{LiF}$, $\text{NaF}$, $\text{KZnF}_3$, $\text{KMgF}_3$, $\text{CsCaF}_3$, $\text{CsCdF}_3$, or $\text{AgCl}$ initially doped with Ni\(^{2+}\) and subsequently irradiated with X-rays or UV rays. Nevertheless, in Bridgman-grown crystals of NaCl doped with divalent nickel, EPR experiments by Shengelaya et al.\(^15\) have undoubtedly proven the formation of Ni\(^{+}\) impurities without irradiating the samples. Such impurities are likely formed through chemical reactions at a temperature of $\sim 1100$ K during the purification process of the molten salt.\(^15\) This is the reason why the Ni\(^{+}\) ions formed in this way easily replace a host Na\(^+\) cation in the NaCl lattice without having a close vacancy. Thus, at variance with what happens for LiF:Ni\(^{+}\), $\text{KMgF}_3$:Ni\(^{+}\), $\text{CsCaF}_3$:Ni\(^{+}\), or $\text{CsCdF}_3$:Ni\(^{+}\), only one Ni\(^{+}\) center is formed in the samples of NaCl:Ni\(^{+}\) explored by Shengelaya et al.\(^15\) This is thus an important reason for choosing NaCl:Ni\(^{+}\) among the different JT systems involving Ni\(^{+}\).

The $g$ tensor of NaCl:Ni\(^{+}\) measured at $T = 20$ K ($g_{||} = 2.86$; $g_\perp = 2.10$) undoubtedly proves\(^11\) that the equilibrium geometry corresponds to an elongated octahedron, although no precise information on the equilibrium $R_{\text{eq}}$ and $R_{\text{ad}}$ values can be derived from it. However, this static spectrum starts to disappear at $T_1 = 35$ K in the X band, while an isotropic spectrum with $g = 2.40$ is already observed at 55 K.\(^15\) Thus, both the low value of $T_1$ and the high value of $g_{||} - g_\perp$ strongly suggest that the barrier between two equivalent distortions is certainly small because $B$ is roughly proportional\(^35\) to $T_1/L(g_{||} - g_\perp)$. For comparison, in NaCl:Ag\(^{2+}\), where $g_{||} = 2.198$ and $g_\perp = 2.041$,\(^6,10\) $T_1 = 95$ K, while the calculated $B$ value is equal\(^35\) to 500 cm$^{-1}$. In KCl:Ag\(^{2+}\), whose $g$ tensor is very close to that measured for NaCl:Ag\(^{2+}\), it is found\(^35\) that $B = 1024$ cm$^{-1}$, which is consistent with a higher $T_1 = 160$ K value.\(^16\)

Bearing these facts in mind, the present work is addressed to explore the system NaCl:Ni\(^{+}\) by means of ab initio calculations based on density functional theory (DFT), together with an analysis of the results, seeking to clarify the mechanisms responsible for the energy barrier. In particular, aside from determining the equilibrium geometry, we want to understand quantitatively why the barrier in NaCl:Ni\(^{+}\) is seemingly much smaller than that for Ag\(^{2+}\), Cu\(^{2+}\), or Rh\(^{2+}\), and thus the anisotropy of the equilibrium geometry of Cu\(^{2+}\) complexes has previously been suggested by several authors.\(^24-28\)
than those involving divalent or trivalent transition-metal impurities.

This work is arranged as follows. Details on the calculation procedure are given in section 2, while the main results obtained in the present work are shown in section 4. In that section, particular attention is paid to exploring the energy, \( E(A_{\mu}) \) and \( E(B_{\mu}) \), of both \( A_{\mu} \) and \( B_{\mu} \) electronic states as a function of the \( Q_\beta \) coordinate. Seeking to clear out the mechanism responsible for the barrier, \( B_\beta \), in NaCl:Ni\(^{+}\), such dependencies are analyzed following the procedure\(^{35}\) employed in an analysis of cluster calculations on NaCl:Rh\(^{3+}\). For the sake of completeness, a recall of that procedure is previously given in section 3.

2. COMPUTATIONAL DETAILS

2.1. Periodic Calculations. Periodic ab initio calculations based on DFT have been carried out on the NaCl:Ni\(^{+}\) system in order to obtain the optimized geometries of the tetragonal elongated and compressed conformations of the JT center and thus the energy barrier between them. All calculations have been performed on \( 2 \times 2 \times 2 \) conventional supercells (which comprise 64 ions), where the Ni\(^{+}\) impurity replaces a Na\(^{+}\) ion of the lattice.

Most calculations were performed with the CRYSTAL09 package that employs localized Gaussian-type orbital (GTO) basis sets to represent the Bloch orbitals.\(^{37}\) Because the energy barrier, \( B_\beta \), between elongated and compressed conformations of the NiCl\(_6^{2-}\) complex in NaCl is expected to be very small, basis sets of different qualities as well as various exchange-correlation functionals have been employed. With regard to the basis sets, most of the calculations have been performed using the pob-TZVP-2012 functions, recently optimized by Peintinger, Vilela Oliveira, and Bredow,\(^\text{38}\) which are all-electron with triple-\(\zeta\) valence with polarization quality. For the sake of comparison, other basis sets of lesser quality have also been used,\(^{39}\)–\(^{41}\) which can be taken from the CRYSTAL database.\(^{42}\) Concerning the exchange-correlation functionals, we have used the following ones: Perdew–Zunger parametrization of the Ceperley–Alder free-electron gas correlation results in the local density approximation\(^{43}\) (LDA); a PBEsol functional designed specifically to improve the generalized gradient approximation (GGA) in solids.\(^{44}\) Apart from these, we have also employed hybrid functionals (with respectively 16% and 20% of Hartree–Fock exchange) such as the B1WC\(^{45}\) and PW1PW.\(^{46}\) These hybrid functionals allow one to obtain geometries, band gaps, and thermochemistry properties with great accuracy and reliability without the need for semiempirical parameters like in DFT+U procedures.

We have employed a \( 4 \times 4 \times 4 \) \( k \)-point mesh, and the structures have been relaxed until a maximum force value below 0.02 eV/Å and a total energy change below \( 10^{-5} \) eV was obtained. It is worth noting that, contrary to what is usually found, the periodic calculations on NaCl:Ni\(^{+}\) made with LDA and GGA functionals converge very slowly and thus are much more expensive than those performed with hybrid functionals.

For checking the reliability of the calculations, the equilibrium lattice parameter, \( a \), and band gap, \( E_g \), of pure NaCl have been first computed using the previously indicated basis sets and functionals. The results are compared with the experimental values\(^{47}\) extrapolated to \( T = 0 \) K, \( a = 5.57 \) Å, and \( E_g = 8.5 \) eV.\(^{48}\) As usual, LDA and GGA-PBEsol methods systematically underestimate the \( a \) and \( E_g \) values, while the best results are found using the B1WC hybrid functional and the basis sets of higher quality, pob-TZVP-2012, \( a = 5.36 \) Å and \( E_g = 7.8 \) eV.

Additional geometry optimizations were carried out by means of the Quantum-Espresso code,\(^{49}\) which uses delocalized plane waves as basis set functions. The kinetic energy cutoff for the wave functions was 40 hartree. The exchange-correlation energy has been computed with the GGA-Perdew–Burke–Emzerhof (PBE) functional\(^{51}\) using ultrasoft pseudopotentials. The \( k \)-point grid was reduced to just the \( \Gamma \) point, although we have verified that with and increase in the grid, the results do not change. The structures were relaxed until a maximum force value below 0.03 eV/Å.

2.2. Cluster Calculations. We have also carried out DFT calculations using the cluster approximation. Calculations have been performed by means of the Amsterdam Density Functional (ADF) code,\(^{52}\) version 2010, on clusters of 39, 87, and 123 atoms. To check the reliability of the present results, calculations have been performed using different exchange-correlation functionals. Among others, we have employed the Becke–Perdew (BP86)\(^{53,54}\) and the PBE\(^{51}\) functionals in the GGA. Moreover, some spin-unrestricted calculations have been performed using the B3LYP hybrid functional\(^{55}\) with 20% of Hartree–Fock exchange.

All atoms have been described through basis sets of TZP quality (tripe-\(\zeta\) Slater-type orbitals plus one polarization function) given in the program database and large frozen core (1s–2p orbitals for Cl and Na and 1s–3p for Ni). In the case of the B3LYP hybrid functional, all-electron calculations have been carried out. In the geometry optimizations, the positions of all ions, except first-shell Cl\(^{-}\) ones and second neighbors Na\(^{+}\) in (100) directions, have usually been kept at their lattice positions. To verify the reliability of this approximation, a calculation on a 123-ion cluster has been carried out, allowing relaxation of the 33 ions not belonging to the surface. We have verified that the relaxation of all ions lying outside the Cl\(^{-}\) ligands is always smaller than 1%.

In all cluster calculations, the effects of the Coulomb potential, \( V_C(r) \), due to the rest of the lattice on the electrons in the cluster have been taken into account. Such a potential is calculated in a first step by means of the Ewald method and is reproduced in a second step by means of a set of point charges, lying outside the cluster and kept at their host lattice positions, whose values are fitted to reproduce the right \( V_C(r) \) potential inside the cluster.\(^{6,56}\) For instance, in the case of the cluster containing 87 atoms (Figure 2), nine ion shells lying outside the cluster, involving 218 point charges, have been employed to reproduce \( V_C(r) \) in 2000 points inside a sphere containing the cluster. The values of all charges belonging to a given shell are taken to be the same. We have verified that the difference between the exact \( V_C(r) \) potential, calculated through the Ewald method, and that derived using the nine shells of point charges is always smaller than 0.02%.

As a test of the reliability of the methodology used, the calculated value for the Na–Cl distance, \( R_{Na-Cl} \), for the pure NaCl lattice, using the GGA-BP86 exchange-correlation functional, was 2.824 Å, which differs...
by less than 1.4% from the experimental figure. Similar results are found for the other cluster calculations.

More details on the cluster calculations, as well as the optimized geometries, are shown in the Supporting Information.

3. ANALYSIS OF THE CALCULATED $Q_6$ DEPENDENCE OF $E(A_{1g})$ AND $E(B_{1g})$ ENERGIES

The physics of $E_g \otimes e_g$ JT systems is essentially driven by expansion of the Hamiltonian in terms of the $Q_6 (\sim 3z^2 - r^2)$ and $Q_4 (\sim x^2 - y^2)$ distortion coordinates:

$$H = H_0 + W_1(r) Q_0 + W_2(r) Q_4 + W_3(r) \cases{Q_4^2 - Q_6^2 &} + W_4(r) (2Q_0 Q_4)$$

$$+ W_5(r) (Q_0^2 + Q_6^2) + W_6(r) (Q_0^3 - 3Q_0 Q_4 Q_6)$$

$$+ \cdots$$

(1)

Here $H_0$ is the adiabatic Hamiltonian for octahedral symmetr.

The second and third terms describe the linear JT coupling, while those involving $W_2(r)$ and $W_4(r)$ correspond to the second-order JT coupling. Because operators $W_1(r)$ and $W_2(r)$ transform like $3z^2 - r^2$ and $W_3(r)$ and $W_5(r)$ transform like $x^2 - y^2$, these terms act in a different way on the wave functions of the electronic doublet and thus have a vibronic character. By contrast, $W_2(r)$ and $W_3(r)$ belong to $A_{1g}$ and the corresponding terms reflect the elastic and anharmonic contributions for the $e_g$ mode, which are the same for the two wave functions of the electronic doublet.

When $Q_4 = 0$ and $Q_6 \neq 0$, the octahedron is tetragonally deformed. The relationship between the $Q_6$ coordinate and the axial, $R_{ax}$ and equatorial, $R_{eq}$ metal–ligand distances of the distorted MX$_6$ complex is given by:

$$Q_6 = \frac{2}{\sqrt{3}} (R_{ax} - R_{eq})$$

(2)

In an $E_g \otimes e_g$ JT problem, it is found that a minimum and a saddle point of the global energy surface can be found in the cross section where $Q_6 = 0$ (see Figure 1). In a previous work analyzing the different factors contributing to the barrier, $B$, we showed that when the $E_g$ term of an octahedral $d^9$ complex splits because of distortion in the $Q_6$ coordinate, the energy surfaces of the resulting $A_{1g}$ and $B_{1g}$ electronic states can be written as:

$$E(A_{1g}) = V_{1e} Q_0 + V_{1s} Q_4^2 + V_{3a} Q_0^3 + \{V_{2e} + V_{PJT}(A_{1g})\} Q_0^2 + \cdots$$

$$E(B_{1g}) = -V_{1e} Q_0 + V_{1s} Q_4^2 + V_{3a} Q_0^3 + \{V_{2e} + V_{PJT}(B_{1g})\} Q_0^2 + \cdots$$

(3)

The linear terms in eqs 3 and 4, involving the $V_{1e}$ constant, come from the linear $W_1(r)$ JT operator in eq 1, using, in first-order perturbation, the frozen wave functions corresponding to the octahedral situation ($Q_6 = Q_4 = 0$). The terms containing $V_{2e}$ and $V_{3a}$ come from the elastic and anharmonic contributions in eq 1, respectively. Because $Q_6 > 0$ represents an elongated octahedron, the anharmonic term favors an elongated conformation when $V_{3a} < 0$. The contributions to eqs 3 and 4 involving $V_{2e}$ arise from the second-order JT coupling in eq 1. With regard to the term $V_{PJT}(i)$ ($i = A_{1g}$, $B_{1g}$), it describes the energy lowering in the $A_{1g}$ and $B_{1g}$ states of the electronic doublet due to interaction with excited states through the linear JT operator in eq 1 in second-order perturbations. This mechanism of energy lowering is sometimes termed the pseudo-JT effect.

If we only consider the excited states arising from the $e_g^4$ configuration for NaCl:Ni$^+$, the difference between $V_{PJT}(A_{1g})$ and $V_{PJT}(B_{1g})$ can be understood by looking at Figure 3, taking into account that the 4s orbital can only be coupled to the $3z^2 - r^2$ one through the $W_1(r)$ operator. As in the $B_{1g}$ state there are two electrons in the $a_{1g}^*(\sim 3z^2 - r^2)$ orbital and only one in the $A_{1g}$ state (Figure 3) the energy gain due to this mechanism for $B_{1g}$ is essentially twice that for $A_{1g}$.

$$V_{PJT}(B_{1g}) = 2V_{PJT}(A_{1g}) = V_{ds}$$

(5)

$$V_{ds} = - \frac{|\langle \phi_0(3z^2 - r^2) | W_1(r) | \phi_0(4s) \rangle|^2}{\Delta_{ds}}$$

(6)

Here $\Delta_{ds} > 0$ means the energy difference between the mainly 4s orbital and $a_{1g}^*(\sim 3z^2 - r^2)$ when $R_{ax} = R_{eq}$. Therefore, the 3d($3z^2 - r^2$)−4s vibronic mixing favors a $B_{1g}$ ground state and thus an elongated geometry. It should be noted that, according to eqs 3–6, the vibronic 3d($3z^2 - r^2$)−4s mixing induces a softening of the force constant especially for the $B_{1g}$ state. Generally, vibronic interactions are responsible for the softening of a force constant, $K$, in the electronic ground state. If $K < 0$ for a nonsymmetric vibration, the structure is no longer stable.

To obtain reliable values of the quantities involved in eqs 3 and 4, it is useful to deal with the $E(A_{1g}) + E(B_{1g})/2$ and $E(A_{1g}) - E(B_{1g})/2$ quantities whose expressions, according to eqs 3 and 4, are given by:

$$\frac{E(A_{1g}) + E(B_{1g})}{2} = \frac{V_{2e} Q_0^2 + V_{3a} Q_0^3}{2}$$

$$\frac{E(A_{1g}) - E(B_{1g})}{2} = \frac{V_{1e} Q_0 + V_{1s} Q_4^2 + V_{3a} Q_0^3}{2}$$

(7)

$$V_{2e} = V_{2e} + \frac{3}{2} V_{ds}$$

$$V_{2e} = -V_{2e} + \frac{1}{2} V_{ds}$$

(8)

If, for instance, the equilibrium geometry of the MX$_6$ complex ($M = d^9$ ion) placed in a cubic lattice is elongated, there are three equivalent distortions characterized by $\{Q_6 = \rho_{6i}; Q_4 = 0\}$, $\{Q_6 = -(1/2)\rho_{6i}; Q_4 = \sqrt{3/2}\rho_{6i}\}$, and $\{Q_6 = -(1/2)\rho_{6i}; Q_4 = -\sqrt{3/2}\rho_{6i}\}$. The energy barrier, $B_i$ between two equivalent distortions is just given by the energy difference of a
compressed complex at its equilibrium geometry (at \(Q_0 = -\rho_{j}\) \(Q_0 = 0\)) and that corresponding to an elongated one computed at \(Q_0 = \rho_{j}\) \(Q_0 = 0\). Thus, according to eqs 3 and 4, B is given by

\[
B = E(A_{1g}; \rho = -\rho_{j}) - E(B_{1g}; \rho = \rho_{j})
\]

\[
= -V_{1c}(\rho_{j} - \rho_{j}) + V_{2a}(\rho_{j} - \rho_{j})^2 - V_{3a}(\rho_{j}^3 + \rho_{j}^3)
\]

\[
- V_{ds}(2\rho_{j}^2 - \rho_{j}^2) + V_{2u}(\rho_{j}^2 + \rho_{j}^2)
\]  

(11)

Therefore, if \(\rho_{j} = \rho_{0}\) the barrier is determined by the anharmonic term and those involving \(V_{ds}\) and \(V_{2u}\). It has previously been shown\(^{11}\) that \(V_{2u}\) is negligible with respect to the pseudo-JT contribution in eqs 3 and 4. Moreover, if in the present case the pseudo-JT coupling is overwhelmingly dominated by the 3d(3\(z^2-r^2\))−4s vibronic mixing, then we can expect that

\[
V_{2e}^{\text{eff}} = \frac{1}{2} V_{ds}
\]

(12)

It is worth noting that, in order to test the validity of eq 12, \(V_{2u}\) can be estimated from the 4s admixture into the 3d(3\(z^2-r^2\)) level calculated for different \(Q_{0}\) distortions. Indeed, the \(1\) \(\phi_{0}(\rho)\) orbital for \(R_{eq} = R_{ds}\) becomes \(\psi(3\(z^2-r^2\))\) when \(Q_{0} \neq 0\), where

\[
\psi(3\(z^2-r^2\)) = \psi(\rho) + \mu(Q_{0}) \psi(4s)
\]

(13)

\[
\mu(Q_{0}) \equiv -\frac{\langle \phi_{0}(\rho)|W_{2e}(r)|\psi(4s)\rangle}{\psi(Q_{0})}
\]

(14)

Of course, \(\psi(4s)\) is not a pure 4s wave function of nickel but involves admixtures of orbitals belonging to ligand ions. For simplicity, let us write

\[
\psi(4s) = \alpha_{4s} s + \beta|\chi\rangle
\]

(15)

Here \(\alpha_{4s}^2\) reflects the 4s admixture in \(\psi(4s)\), while the second term shortly describes the other contributions. In the calculations, it is relatively easy to determine the amount, \(f_{2e}(Q_{0})\), of 14s in \(\phi_{0}(3\(z^2-r^2\))\), which, according to eqs 13−15, is just given by

\[
f_{2e}(Q_{0}) \equiv \mu(Q_{0})^2 \alpha_{4s}^2
\]

(16)

Therefore, \(V_{2e}\) can be estimated from the calculated \(f_{2e}(Q_{0})\) curve and the \(\Delta_{ds}\) value through the expression

\[
V_{2e} = -\left[\frac{f_{2e}(Q_{0})}{\alpha_{4s}^2}\right] \Delta_{ds}
\]

(17)

Because the results obtained on NaCl:Ni\(^{2+}\) are compared with those\(^{11,13,36}\) for NaCl:Rh\(^{2+}\) where there is only one unpaired electron in the \(3d\) shell, the corresponding expressions for \(E(A_{1g})\) and \(E(B_{1g})\) are

\[
E(A_{1g}) = -V_{1c}Q_{0} + V_{2a}Q_{0}^2 + V_{3a}Q_{0}^3 + [V_{2e} + V_{ds}]Q_{0}^2
\]

+ \ldots

(18)

\[
E(B_{1g}) = V_{1e}Q_{0} + V_{2a}Q_{0}^2 + V_{3a}Q_{0}^3 + V_{2s}Q_{0}^2 + \ldots
\]

(19)

Thus if \(V_{2a}\) and \(V_{ds}\) are both negative, they favor an elongated geometry for NaCl:Rh\(^{2+}\), where the unpaired electron is placed in the \(a_{1g}\) \((3z^2-r^2)\) orbital. This situation has been well observed experimentally.\(^{18}\)

4. RESULTS AND DISCUSSION

In a first step, we have calculated the equilibrium Ni\(^{2+}\)−Cl\(^{−}\) distance, \(R_{eq}\), for the average \((3z^2-r^2), (2x^2-y^2), (x^2-y^2)\) configuration.\(^{8,11}\) Because in this configuration the two orbitals are equally populated, there is no JT effect like happens for the ground state of Ni\(^{2+}\) in octahedral coordination. All performed calculations using different methods, functionals, and basis sets lead to similar results. For example, the value \(R_{eq} = 2.69 \text{ Å}\) derived using a 87-atom cluster, the GGA-BP86 functional,\(^{53,54}\) and relaxing only the ligand shell is found to be only 1 pm smaller than that coming from a 64-atom supercell calculation and the hybrid B1WC functional.\(^{46}\) This result points out that the Na\(^{+}\)→Ni\(^{2+}\) substitution induces a small inward relaxation of 4% and suggests an ionic radius of 0.90 Å for Ni\(^{2+}\). This figure is thus consistent with a previous estimation.\(^{59}\) Additional calculations on a 87-atom cluster have been performed where the distance \(R(Ni−Na)\) between the impurity and closest Na\(^{+}\) ion along (100) directions has also been taken as variable in the minimization procedure. The calculated equilibrium distance \(R(Ni−Na) = 5.59 \text{ Å}\) is found to be only 1% smaller than the lattice parameter \(a = 5.64 \text{ Å}\). Thus, the mismatch due to the slightly different ionic radius of Na\(^{+}\) and Ni\(^{2+}\) mainly affects the average Ni\(^{2+}\)−Cl\(^{−}\) distance.

In a second step, we have been working with the real \((3z^2-r^2), (2x^2-y^2), (x^2-y^2)\) \((B_{1g}\) state) and \((3z^2-r^2), (x^2-y^2)\) \((A_{1g}\) state) configurations, paying particular attention to obtaining the equilibrium geometry for the elongated and compressed conformations and also the corresponding energy difference, \(B\). For clarifying this matter, a considerable number of periodic and cluster calculations have been performed by varying the basis set, the employed functional, and the cluster size. As a salient feature, we have found that in all performed calculations the \(B_{1g}\) value for NaCl:Ni\(^{2+}\) is less than 160 cm\(^{-1}\), thus certainly smaller than the values derived for NaCl:Rh\(^{2+}\) \((B = 511 \text{ cm}^{-1})\)\(^{11,13}\) NaCl:Ag\(^{2+}\) \((B = 500 \text{ cm}^{-1})\), or KCl:Ag\(^{2+}\) \((B = 1024 \text{ cm}^{-1})\)\(^{35}\).

Values of the equilibrium \(R_{eq}\) and \(R_{ds}\) distances for both the \(B_{1g}\) and \(A_{1g}\) states and the barrier \(B\) derived through representative periodic supercell and cluster calculations are gathered in Tables 1 and 2, respectively. In the case of periodic calculations, most of the values obtained with the best basis set give rise to positive \(B\) values in the range 80−120 cm\(^{-1}\). We have verified that when the quality of the basis set is reduced, negative \(B\) values are more frequently encountered.

A similar picture emerges when looking at cluster calculations. Interestingly, the obtained value of \(B\) is found to be little dependent on the cluster size, and so in the clusters containing 39, 87, and 123 atoms, the value of \(B\) is always lying in the range 70−96 cm\(^{-1}\), keeping the same functional and basis set (Table 2). As happens in the case of periodic calculations, a change of the functional can lead to the appearance of negative \(B\) values although \(B_{1g}\) is found to be always smaller than 160 cm\(^{-1}\). In particular, this situation is found using the B3LYP functional in a spin-unrestricted calculation such as is shown in Table 2. It is worth noting that because \(B_{1g}\) is small it is not surprising that some calculations yield negative \(B\) values. A similar situation is encountered for CaO:Ag\(^{2+}\), where experimental results\(^{60}\) are consistent with a static JT effect and an elongated equilibrium geometry while ab initio calculations\(^{61,63}\) gave \(B = -135 \text{ cm}^{-1}\).
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Table 1. Results of Periodic Supercell Calculations for the NaCl:Ni⁺ Center in the B₁g and A₁g States, Using Different Functional and Basis Sets

<table>
<thead>
<tr>
<th>basis set</th>
<th>functional</th>
<th>state</th>
<th>R_\text{eq} (Å)</th>
<th>R_\text{ax} (Å)</th>
<th>Q_δ</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>GTO</td>
<td>hybrid PW1PW</td>
<td>B₁g</td>
<td>2.560</td>
<td>2.845</td>
<td>0.329</td>
<td>+120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A₁g</td>
<td>2.723</td>
<td>2.529</td>
<td>-0.224</td>
<td></td>
</tr>
<tr>
<td>GTO</td>
<td>hybrid B1WC</td>
<td>B₁g</td>
<td>2.523</td>
<td>2.828</td>
<td>0.352</td>
<td>+80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A₁g</td>
<td>2.679</td>
<td>2.497</td>
<td>-0.210</td>
<td></td>
</tr>
<tr>
<td>GTO</td>
<td>LDA</td>
<td>B₁g</td>
<td>2.487</td>
<td>2.784</td>
<td>0.343</td>
<td>+112</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A₁g</td>
<td>2.625</td>
<td>2.454</td>
<td>-0.197</td>
<td></td>
</tr>
<tr>
<td>GTO</td>
<td>GGA-PBEsol</td>
<td>B₁g</td>
<td>2.512</td>
<td>2.811</td>
<td>0.345</td>
<td>-160</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A₁g</td>
<td>2.667</td>
<td>2.460</td>
<td>-0.240</td>
<td></td>
</tr>
<tr>
<td>PW</td>
<td>GGA-PBE</td>
<td>B₁g</td>
<td>2.503</td>
<td>2.886</td>
<td>0.442</td>
<td>+8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A₁g</td>
<td>2.730</td>
<td>2.458</td>
<td>-0.314</td>
<td></td>
</tr>
</tbody>
</table>

Here GTO corresponds to the recently published pob-TZVP-2012 Gaussian basis set 56 for the CRYSTAL code, while PW means a plane-wave basis set in the Quantum-ESPRESSO code. 57 R_\text{eq} and R_\text{ax} are the equilibrium equatorial and axial Ni⁺−Cl⁻ distances (in Å) and B is the energy barrier (in cm⁻¹) between the A₁g and B₁g states. Values of the Q_δ coordinate at equilibrium (in Å) are also reported.

Table 2. Representative Values of the Equilibrium R_\text{eq} and R_\text{ax} Distances (in Å) for Both the B₁g and A₁g States and the Energy Barrier, B (in cm⁻¹), for NaCl:Ni⁺ Calculated by Means of Clusters of 39, 87, and 123 Atoms

<table>
<thead>
<tr>
<th>size</th>
<th>functional</th>
<th>state</th>
<th>R_\text{eq} (Å)</th>
<th>R_\text{ax} (Å)</th>
<th>Q_δ</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td>GGA-BP86</td>
<td>B₁g</td>
<td>2.562</td>
<td>2.901</td>
<td>0.391</td>
<td>+96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A₁g</td>
<td>2.783</td>
<td>2.491</td>
<td>-0.34</td>
<td></td>
</tr>
<tr>
<td>87</td>
<td>GGA-BP86</td>
<td>B₁g</td>
<td>2.575</td>
<td>2.858</td>
<td>0.327</td>
<td>+74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A₁g</td>
<td>2.767</td>
<td>2.497</td>
<td>-0.312</td>
<td></td>
</tr>
<tr>
<td>123</td>
<td>GGA-BP86</td>
<td>B₁g</td>
<td>2.563</td>
<td>2.873</td>
<td>0.358</td>
<td>+88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A₁g</td>
<td>2.767</td>
<td>2.483</td>
<td>-0.327</td>
<td></td>
</tr>
<tr>
<td>87</td>
<td>GGA-PBE</td>
<td>B₁g</td>
<td>2.589</td>
<td>2.870</td>
<td>0.324</td>
<td>+55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A₁g</td>
<td>2.772</td>
<td>2.526</td>
<td>-0.28</td>
<td></td>
</tr>
<tr>
<td>87</td>
<td>B3LYP</td>
<td>B₁g</td>
<td>2.648</td>
<td>2.861</td>
<td>0.25</td>
<td>-140</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A₁g</td>
<td>2.797</td>
<td>2.595</td>
<td>-0.23</td>
<td></td>
</tr>
</tbody>
</table>

These results have been obtained using the BP86 functional 55,54 and also the PBE 51 and B3LYP 55,56 functionals. The value of the Q_δ coordinate at equilibrium (in Å) is also reported.

As to the experimental g tensor of NaCl:Ni⁺ at T = 20 K, the values g∥ = 2.86 and g⊥ = 2.10 prove 15 that the unpaired electron is placed in the b₁g*(~x²−y²) orbital and thus B is positive.

With regard to the equilibrium R_\text{eq} and R_\text{ax} values calculated for both the B₁g and A₁g states using different procedures (Tables 1 and 2), it can be seen that there is a reasonable agreement among them. Nevertheless, variation of the calculated R_\text{eq} and R_\text{ax} values reported on Tables 1 and 2 shows differences up to 4%. For comparison, cluster and periodic supercell calculations on MgO:Cr³⁺ using different types of functionals and changing the number of involved ions all lead 16 to the same value of the Cr³⁺−O²− distance within 0.8%. This underlines the difficulties for studying the Ni⁺ impurity in comparison with Cr³⁺, where the 3d−4s separation amounts 10 to 14 eV.

In the past, we have formulated the equations for d−d transitions in NaCl:Ni⁺ at the corresponding equilibrium geometry. The results for the a₁g*(~3z²−r²) → b₁g*(~x²−y²), b₂g*(~xy), and e₁g*(~x²z²−y²z²) → b₁g* transition energies (called Δ₁, Δ₂, and Δ₃, respectively) are collected in Table 3 together with the energy for the first allowed charge-transfer transition e₁g*(π) → b₁g*. Such figures are compared with experimental values measured 62−64,65 for CdCl₂⋅Cu⁺ 24 and KCl⋅Ag⁺ 66. It can be noticed that Δ₁, Δ₂, and Δ₃ values are much smaller for NaCl:Ni⁺ than for other divalent 3d⁹ and 4d⁹ cations, stressing the singularity of the monovalent Ni⁺ ion. In fact, the calculated Δ₁ value for NiCl₂⁺ in NaCl is around one-third that measured 64 for the CuCl₂⁴⁺ complex in CdCl₂, pointing out that no Dq decreases upon passing from trivalent to divalent impurities 65 and especially from the last ones to monovalent cations. Along this line, a value Δ₁ = 4700 cm⁻¹ was estimated 54 for AgCl:Ni⁺.

Although no optical measurements on the d−d transitions of Ni⁺ impurities in insulators have hitherto been reported, the results collected in Table 3 are qualitatively consistent with the high g∥ = 2.86 value measured 15 for NaCl:Ni⁺ compared with g∥ = 2.84 3 derived 69 for CdCl₂⋅Cu⁺ because g∥ = 2.86 depends in second-order perturbation 70,71 on (Δ₁)². Furthermore, using the general expressions for g∥ = 2.86 and g∥ = 2.84 given in ref 68, the geometry optimized in the periodic PW1PW calculations, the Δ₁ and Δ₂ values of Table 3, and the covalency coefficients also derived from the present calculations, we have found g∥ = 2.89 and g∥ = 2.84 in ref 68, the geometry optimized in the periodic PW1PW calculations, the Δ₁ and Δ₂ values of Table 3, and the covalency coefficients also derived from the present calculations, we have found g∥ = 2.89 and g∥ = 2.84. Such values are thus not far from the experimental figures. 15 With regard to the covalency, if we simply write the normalized wave function of the antibonding b₁g*(~x²−y²) orbital as

\[ \left| b₁g* \right| (x²−y²) = α|3d(x²−y²)| - β|g₁g*| \]

we have found α² = 0.90 for NiCl₂⁺ in NaCl, thus pointing out that the unpaired electron is essentially residing on the central cation, while a higher covalency is obtained 65 for CuCl₂⁺ (α² = 0.70) and especially for AgCl₂⁺ where α² = 0.50. 60 In eq 20, |g₁g*| shortly denotes a linear combination of 3p and 3s orbitals of equatorial Cl⁻ ligands. The increase of covalency upon passing from NiCl₂⁺ to AgCl₂⁺ is qualitatively consistent with the significant decrease of the energy of the first allowed charge-transfer transition e₁g*(π) → b₁g* (Table 3). Accordingly, the optical electronegativity 70,72,74 x_{opt} of Ni⁺ should be around 1.1. The singularity of the monovalent Ni⁺ ion is obvious when comparing this value with the empirical values estimated by Jørgensen 73 for Ni²⁺ and Cu⁺, x_{opt} = 2.2 and 2.4, respectively, or the obtained 75,76 for Ag⁺ and Rh⁺, x_{opt} = 2.8 and 2.5, respectively.

Concerning the barrier, B, a rough estimation of this quantity for NaCl:Ni⁺ can be obtained from temperature T = 35 K at which the static spectrum starts to disappear 65 in conjunction with the optical data.
with the calculated value\textsuperscript{15} $B = 500$ cm\textsuperscript{-1} for NaCl:Ag\textsuperscript{2+} and the corresponding experimental value\textsuperscript{16} $T_1 = 95$ K also measured in X-band EPR experiments. Let us denote by $\nu$ the jump frequency between two equivalent minima separated by the barrier $B$. Assuming an Arrhenius type law for the temperature dependence of $\nu$, it can be written as

$$\nu = \nu_0 e^{-B/kT}$$  \hspace{1cm} (21)

The transition between a static EPR spectrum and an average isotropic one requires that\textsuperscript{9,35}

$$h\nu \approx (g_i \parallel g_\perp) \beta H$$  \hspace{1cm} (22)

where $\beta$ denotes the Bohr magneton. Then, because $H \approx 300$ mT (X band) and $g_i - g_\perp = 0.155$ for NaCl:Ag\textsuperscript{2+}\textsuperscript{16} if we noting that the value $\nu$ for NaCl:Ni\textsuperscript{+} is much smaller than those derived for Ag\textsuperscript{2+},\textsuperscript{1,13} To achieve this goal, we have analyzed the results derived for NaCl:Ni\textsuperscript{+} with a positive $B$ shown here have been derived through a calculation on the 87 ions (Figure 3), giving $B(\text{NaCl:Ni}^+) \approx 120$ cm\textsuperscript{-1}. Thus, the positive $B$ values obtained in periodic and cluster calculations (Tables 1 and 2) are compatible with this estimation.

A central matter in this research is to understand why the $B$ value for NaCl:Ni\textsuperscript{+} is much smaller than those derived for Ag\textsuperscript{2+}-doped NaCl and KCl\textsuperscript{35} and for NaCl:Rh\textsuperscript{2+} \textsuperscript{11,13}. To achieve this goal, we have analyzed the results derived for NaCl:Ni\textsuperscript{+} with a 87-ion cluster (Figure 3), giving $B = 74$ cm\textsuperscript{-1} (Table 2), by means of the procedure explained in section 3.\textsuperscript{11} It is worth noting that the value $Q_\beta = 0.327$ Å derived for the elongated conformation of NaCl:Ni\textsuperscript{+} (Table 2) is practically coincident with $Q_\beta = 0.320$ Å obtained\textsuperscript{11,13,36} for NaCl:Rh\textsuperscript{2+}. This implies that knowledge of the magnitude of the distortion alone does not allow prediction of the value of $B$.

Seeking to clear out this matter, the calculated $E(A_{1g}, Q_\beta)$ and $E(B_{1g}, Q_\beta)$ curves, displayed in Figure 4, have been explored through the procedure explained in section 3.\textsuperscript{11} From the calculated $[E(A_{1g}) + E(B_{1g})]/2$ and $[E(A_{1g}) - E(B_{1g})]/2$ quantities, the values of $V_{1e}$, $V_{2e}$, $V_{3e}$, and $V_{4e}$ have been determined. The main results obtained for NaCl:Ni\textsuperscript{+} are collected in Table 4, where they are compared to those\textsuperscript{11,13,36,52} for NaCl:Rh\textsuperscript{2+}. It can be noticed that while for NaCl:Rh\textsuperscript{2+} the curvature at the minimum of the compressed geometry is clearly higher than that for the elongated conformation,\textsuperscript{58} this is not true for NaCl:Ni\textsuperscript{+}.

With regard to calculated values, $V_{1e} = 0.32$ eV/Å derived for NaCl:Ni\textsuperscript{+} is about 4 times smaller than $V_{1e} = 1.40$ eV/Å previously derived\textsuperscript{11} for NaCl:Rh\textsuperscript{2+} (Table 4). This reduction is qualitatively consistent with that experienced by 10Dq upon passing from divalent cations to a monovalent cation like Ni\textsuperscript{+}.

On the other hand, the value $V_{4s} = 0.32$ eV/Å is essentially compatible with the figure $\Delta_0 = 1530$ cm\textsuperscript{-1} given in Table 3 and $Q_\beta = 0.327$ Å because in a first approximation\textsuperscript{11,12}

$$\Delta_0 = 2V_{4s}Q_\beta$$  \hspace{1cm} (23)

It is worth noting that while in comparison to NaCl:Rh\textsuperscript{2+} the values of $V_{2e}$ and $|V_{3e}/V_{4s}|$ obtained for NaCl:Ni\textsuperscript{+} are significantly reduced, this is not the case for the $V_{3a}^0$ quantity. As the obtained value for NaCl:Ni\textsuperscript{+}, $V_{3a}^0 = -0.16$ eV/Å$^2$, is negative, this is qualitatively consistent with the assumption that $V_{3a}^0 = V_{3a}/2$ mainly arises from the 3d(3$z^2-r^2$)\textsuperscript{4s} vibronic coupling because, according to eq 6, $V_{3a} < 0$. Moreover, the term involving $V_{3a}$ in eq 12 gives rise to a barrier $B = 240$ cm\textsuperscript{-1}.

As a salient feature, the sign of the anharmonic coefficient, $V_{4s} = 0.26$ eV/Å\textsuperscript{3}, is found to be positive for NaCl:Ni\textsuperscript{+}, a result that is thus completely at variance with what is found for NaCl:Rh\textsuperscript{2+}, where\textsuperscript{11} $V_{4s} = -1.1$ eV/Å\textsuperscript{2}. This relevant result just means that the equilibrium geometry for NaCl:Ni\textsuperscript{+} would be compressed if only the anharmonic contribution is taken into account. More precisely, with the $Q_\beta$ values given in Table 2, the contribution to the barrier from the $V_{3a}(\rho_3^3 + \rho_4^3)$ term in eq 12 is equal to $-135$ cm\textsuperscript{-1}, while that coming from the first two terms involving the $V_{1e}$ and $V_{2e}$ coefficients is equal only to $-24$ cm\textsuperscript{-1}. These results thus point out that the elongated geometry of the NiCl\textsuperscript{6} complex in NaCl:Ni\textsuperscript{+} is mainly due to the 3d(3$z^2-r^2$)\textsuperscript{4s} vibronic coupling, although its contribution to $B$ is canceled to an important extent by that arising from the anharmonicity. This explains albeit qualitatively the low value of $B$ for NaCl:Ni\textsuperscript{+} in comparison with those obtained\textsuperscript{11,13,36} for NaCl:Rh\textsuperscript{2+}, NaCl:Ag\textsuperscript{2+}, and KCl:Ag\textsuperscript{2+}.

Seeking to test the reliability of the $V_{4e}^0 = V_{4s}/2$ assumption, we have estimated $V_{4s}$ by means of eqs 16 and 18. From our calculations, we have determined the amount, $f_{4s}(Q_\beta)$, of 4s admixture into $|f_\phi(3z^2-r^2)|$. The results in Figure 5 show that $f_{4s}(Q_\beta)$ is actually proportional to $Q_\beta^2$ with $f_{4s}(Q_\beta)/Q_\beta^2 = 0.085$ Å\textsuperscript{-2}. On the other hand, the 4s admixture in $|f_\phi(4s)|$ is found to be $\alpha_{4s}^2 = 0.70$, while the present calculations give $\Delta_0 = 2.5$ eV. Therefore, according to eqs 16 and 18, we estimate $V_{4s} = -0.30$ eV/Å$^2$ and thus $V_{4s}/2$ is close to the value $V_{4e}^0 = -0.15$ eV/Å$^2$ derived from analysis of the results collected in Table 3. This analysis thus strongly supports that the elongated

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
system & $V_{1e}$ & $V_{2e}$ & $V_{3e}$ & $V_{4e}$ & $E_{JT}$ (cm\textsuperscript{-1}) & $B$ (cm\textsuperscript{-1}) \\
\hline
NaCl:Ni\textsuperscript{+} & 0.32 & 0.90 & 0.26 & 0.16 & 534 & 72 \\
NaCl:Rh\textsuperscript{2+} & 1.40 & 2.8 & 1.1 & 0.21 & 1830 & 511 \\
\hline
\end{tabular}
\caption{Values of $V_{1e}$, $V_{2e}$, $V_{3e}$, and $V_{4e}$ Vibronic Constants (in eV/Å, eV/Å$^2$, eV/Å$^3$, and eV/Å$^2$, Respectively) and the Barrier, $B$ (in cm$^{-1}$), Derived for NaCl:Ni\textsuperscript{+} from the Calculation of the 87-Atom Cluster with the GGA-BP86 Functional\textsuperscript{14}}
\end{table}

}\hspace{1cm}
As has been pointed out before, in NaCl:Rh2+ the RhCl₆ positive lattice cation along a to the impurity ion, M, as well as to the closest A host attached figure, a given ligand, X, is depicted in Figure 6. In such a simple model for clarifying the two different situations is a1g (3z²−r²)−4s vibronic coupling.

A central point in the present analysis is to understand why the sign of the anharmonic parameter, V₉ₓ, is found to be positive in NaCl:Ni⁺, while it is clearly negative for NaCl:Rh²⁺. As has been pointed out before, in NaCl:Rh²⁺ the RhCl₆⁻ complex is practically elastically decoupled from the rest of the lattice, while this situation is likely not to be true for NaCl:Ni⁺, where Ni⁺ and Na⁺ are both monovalent ions. A simple model for clarifying the two different situations is depicted in Figure 6. In such a figure, a given ligand, X, is attached to the impurity ion, M, as well as to the closest A host lattice cation along a ⟨100⟩ direction. Let us now consider the geometry obtained for NaCl:Ni⁺ is mainly due to the 3d(3z²−r²)−4s vibronic coupling.

The ligands move along the M–X directions, keeping M and A fixed. In such a case, when a ligand is not in its equilibrium position, there are two springs that are activated. If we consider, in principle, a single M–X–A unit, then the associated potential energy can be described by

\[
U_p(M-X-A) = \frac{1}{2} k(u_x)^2 + \frac{1}{2} k'(u_x)^2 - g(u_x)^3 + g'(u_x)^3
\]

In this expression, uₓ describes the separation of the ligand coordinate along a ⟨100⟩ direction from its equilibrium position. If uₓ > 0, it means that the ligand is moving away from the impurity and thus approaching the A ion. If we assume that the anharmonicity in both the M–X and X–A bonds favors the elongation of both springs, then g and g' must be positive. It should be recalled that in a simple diatomic molecule g > 0 is actually responsible for a positive thermal expansion coefficient.

For this reason, the total anharmonic energy of the M–X–A unit favors a compressed situation in the M–X bond, provided that g' > g. Let us now consider a Qₓ distortion involving the six ligands. Because the anharmonic energy of a single M–X–A unit is equal to (g' − g)uₓ³, Vₓₓ is simply given by

\[
V_{sx} = \frac{1}{\sqrt{12}} (g' - g)
\]

When the complex is elastically decoupled from the rest of the lattice, this implies that k ≫ k' and g ≫ g' and then Vₓₓ is necessarily negative, pointing out that an elongation described by Qₓ yields a smaller energy increase than a −Qₓ compression. By contrast, in a case like NaCl:Ni⁺, where both monovalent ions have a similar ionic radius, the conditions k ≫ k' and g ≫ g' are not necessarily fulfilled.

Seeking to clear out this relevant matter we have estimated from the present calculations the values of the two constants k and k' in eq 21. While k'/k = 0.28 for NaCl:Rh²⁺, a much higher value k'/k = 2.9 has been obtained for NaCl:Ni⁺. This result strongly supports that in the last case the NiCl₆⁻ complex is elastically coupled to the rest of the lattice and thus it can reasonably be expected that g' > g. This reasoning thus explains why Vₓₓ is negative for NaCl:Rh²⁺ while it can be positive for the present case.

5. FINAL REMARKS

According to the present results, the understanding of the actual geometry displayed by a seemingly simple JT system is certainly a nontrivial problem requiring a detailed quantitative study. Indeed, it has been shown that for NaCl:Ni⁺ the two main contributions to the barrier have an opposite sign and thus the calculated |B| value is certainly smaller than B ≈ 500 cm⁻¹ obtained for NaCl:M⁺⁺ (M = Rh, Ag) and B = 1024 cm⁻¹ derived for KCl:Ag⁺. Because of this special situation, it is not surprising to find that some calculations on NaCl:Ni⁺ lead to negative B values, although |B| is always smaller than 160 cm⁻¹.

As a salient feature, the present study supports that the equilibrium elongated geometry observed experimentally for NiCl₆⁻ in NaCl is mainly due to the 3d(3z²−r²)−4s vibronic mixing. To our knowledge, NaCl:Ni⁺ is the first JT system in which it has quantitatively been demonstrated that the dominant contribution to the barrier arises from such a vibronic mixing. This result thus stresses that the barrier in JT systems cannot be understood at all, neglecting the changes of the electronic density accompanying the small distortions.
The present results for NaCl:Ni+ are thus fully different from those found for NaCl:Rh2+11 or KCl:Ag2+3,35 where the barrier comes mainly from the anharmonicity. Therefore, in NaCl:Ni+ the electronic structure of the impurity plays a key role for understanding the equilibrium geometry. Indeed, in the case of free ions, the nd−(n+1)s separation is equal16 to 2 eV for Ni+ (n = 3), 8 eV for Cu2+ (n = 3), 9 eV for Rh2+ (n = 4), 9 eV for Ag2+ (n = 4), and 14 eV for Cr2+ (n = 3).

It is worth noting that EPR data prove that in K2MgF3:Ni+, the local geometry of NiF6−5 corresponds to an elongated octahedron,73 while in K2ZnF4:Cu2+, CuF6−4 is, however, compressed.74,32 Again the small 3d−4s separation in Ni+ has been shown to play a key role for explaining this surprising situation.75

The present analysis supports that in NaCl:Ni+ the anharmonicity of the eg mode alone favors a compressed rather than an elongated geometry. This fact just reflects that the NiCl6−5 complex is not elastically decoupled from the rest of the lattice like when Na+ is replaced by a smaller divalent cation. This situation is thus quite different from that of free molecules subject to the JT effect as discussed in refs 76 and 77.

Although EPR work carried out on KMgF3:Ni+31 or CsCaF3:Ni+32 proves that the JT center formed in these systems exhibits an elongated geometry, it has been assumed by several authors that in LiF:Ni+ and NaF:Ni+ such a center displays a compressed geometry.29,67,78,79 Nevertheless, there are serious arguments against the correctness of this assignment as discussed in refs 80 and 81.

Because of the low values of the barrier in NaCl:Ni+, it is interesting to explore why coherent tunneling is not observed instead of a static JT effect. When coherent tunneling among equivalent distortions takes place, the EPR spectrum exhibits a cubic rather than a tetragonal pattern, a situation termed the dynamic JT effect.9–14 The unavoidable presence of random strains in any real crystal very often destroys the coherence,9 and then an EPR spectrum characteristic of a static JT effect with D1h symmetry is usually observed for d9 ions in cubic halides.10 Calling δ, the energy splitting induced by a tetragonal random strain on the vibronic doublet, the occurrence of a dynamic JT effect requires that 3Γ > δ, where 3Γ is the tunneling splitting13,14 and δ is thus a sample-dependent quantity. Because up to now no direct measurement of 3Γ has been performed for MgO:Cu2+, where a dynamic JT effect has been observed experimentally,82 the situation on the actual value of 3Γ and the ratio δ/3Γ is still controversial. In this sense, Reynolds et al. obtained82 a ratio δ/3Γ = 0.1 from analysis of the available EPR data, while more recently Riley et al.83 give δ/3Γ = 0.5. On the other hand, ab initio results on MgO:Cu2+ give13,14 3Γ = 235 cm−1, while the calculated 3Γ value13,14 for the two other cases50,82 (MgO:Ag2+ and CaO:Cu2+), where a dynamic JT effect has actually been observed, is always higher than 50 cm−1. Furthermore, a theoretical study carried out on MgO:Cu2+ points out that the dynamic JT effect is already destroyed14 when δ/3Γ > 0.2. This standpoint is consistent with the observation60 of a static JT effect in CaO:Ag2+, where the calculated 3Γ value13,14 is equal to 30 cm−1.

With regard to NaCl:Ni+, the calculated kinetic energy for the vibronic ground state13,14 when B = 0, E∥ = 0, is equal to h2/8mB2E∥ = 1.2 cm−1, which is certainly smaller than the actual value of the barrier B. Here MS is the ligand mass and B2E∥ corresponds to the equilibrium Q∥ value for the B2E∥ state.13,14 For this reason, it can reasonably be expected that the actual 3Γ for NaCl:Ni+ will be clearly smaller than 3Γ = 8E∥ = 9 cm−1 calculated13,14 when there is no barrier at all. Thus, the present analysis and the typical values14 of δ, (~10 cm−1) strongly favor the observation of a static JT effect in NaCl:Ni+ in agreement with the experimental data.15

The present results stress the importance of ab initio calculations for reaching a microscopic understanding of mechanisms responsible for the observed equilibrium geometry. In this sense, most of the experimental information on systems displaying a static JT effect corresponds to the electronic ground state. Therefore, although the usual EPR fingerprints17 of elongated (g∥ − g⊥ ≈ 4(g∥ − g⊥)) and compressed (g∥ − g⊥ > 0 and g∥ − g⊥ ≈ 0) conformations for d9 impurities are very different, it is not easy to know the small energy difference between them only from the experimental data. On the other hand, calculations provide insight into the parameters involved in the usual effective JT Hamiltonians, thus avoiding unnecessary speculations in the models.

In conclusion, analysis of the ab initio calculations in JT systems provides very crucial information on the subtle origin of the equilibrium geometry. Further work along this line is now underway.

**ASSOCIATED CONTENT**

Supporting information

More details on the cluster calculations, as well as the optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

Support by the Spanish Ministerio de Ciencia y Tecnología under Projects FIS2012-30996 and FIS2009-07083 is acknowledged. J.M.G.L. acknowledges support from the Spanish Ministry of Economy and Competitiveness under Project FIS2010-21282-C02-01 and through Ramon y Cajal grant RYC-2011-07782.

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