State-Specific Chemical Dynamics of the Nonvalence Bound State of the Molecular Anions

Do Hyung Kang, Jinwoo Kim, Han Jun Eun, and Sang Kyu Kim*

CONSENSUS: Nonvalence bound states (NBS) are anionic states where the excess electron is extremely loosely bound to the neutral core through long-range potentials. In contrast to the valence orbitals of which the electron occupancy determines the molecular structure, as well as the chemical reactivity, the nonvalence orbital is quite diffuse and located far from the neutral core. The NBS can be classified into the dipole-bound state (DBS), quadruple-bound state (QBS), or correlation-bound state (CBS) according to the nature of the electron-neutral interaction, although their interaction potentials may cooperatively contribute. The NBS is ubiquitous in nature and has the strong implications in atmospheric, interstellar, or biological chemistry. Accordingly, NBS has long been conceived to play the role of the doorway into the formation of a stable anion or dissociative electron attachment (DEA). Despite intensive and extensive studies, however, the quantum-mechanical nature of NBS is still far from being thorough understanding. Herein, we describe a new aspect of state-specific NBS-mediated chemical dynamics, which has been revealed through a series of recent studies by our group. We have employed picosecond time-resolved pump–probe spectroscopy combined with cryogenically cooled ion trap and velocity-map imaging techniques to study closed-shell anions generated by electrospray ionization. DBS vibrational Feshbach resonances are prepared by the optical excitation of phenoxide, for instance, and their individual lifetimes have been precisely measured in a state-specific manner to reveal the strong mode-dependency of the autodetachment rate. Fermi's golden rule turns out to be extremely useful for a rational explanation of the experiment, although the more sophisticated theoretical model is desirable for the more quantitative analysis. For the DBS of para-chlorophenoxide or para-bromophenoxide where the polarizability of neutral core is substantial, the Fermi's golden rule based on the charge-dipole potential needs to be significantly modified to include the correlation effects to explain the exceptionally slow autodetachment rates. For the QBS of 4-cyanophenoxide, the mode-specific behavior of the quadrupole ellipsoid tensor explains the strong mode-dependent autodetachment rate. Meanwhile, the nonadiabatic transition of the excess electron into the valence orbital can result in stable anion formation or immediate chemical bond rupture. In the DBS of ortho-, meta-, or para-iodophenoxide, the transformation of the loosely bound excess electron into the σa* antibonding orbital occurs to give I− as a final fragment. The fragmentation mediated by DBS occurs competitively with the concomitant autodetachment, paving a new way of the reaction control by tuning the quantum-mechanical nature of the DBS Feshbach resonance. This experimental observation provides the foremost evidence for the dynamic role of the DBS as a doorway into anion chemistry, such as DEA. The ponderomotive force on the electron in the nonvalence orbital has been demonstrated for the first time in a strong optical field, giving great promise for the manipulation of polyatomic molecules in terms of the spatial location, as well as the AC-Stark control of the chemical reaction.

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**INTRODUCTION**

Although the molecular structure and chemical reactivity are primarily determined by the electronic configurations of the occupied valence orbitals, the excess electron held by the long-range attractive potentials plays a pivotal role in anion chemistry. It is anticipated to be somewhat fragile, the nonvalence bound state (NBS), where the monopole-multipole interaction is largely responsible for the electron binding. Notably, these interactions are sometimes less distinct, as they can cooperatively contribute. Since its first conception by Fermi and Teller, it has been widely accepted that the DBS is likely to be formed when the dipole moment of the neutral core exceeds 2.5 D. For closed-shell anionic species, the DBS is often prepared by the optical excitation of deprotonated anions. Notably, recent spectroscopic studies on cryogenically cooled anions have unraveled the detailed vibrational structures of Feshbach resonances for many interesting chemical and biological systems, whereas femtosecond time-resolved spectroscopic studies have provided an overall picture of the relaxation pathway. Despite a number of elegant experimental and theoretical works to date, however, the state-specific quantum-mechanical nature of the DBS has been considerably less explored, and thus, it is still beyond thorough understanding.

As the excess electron of NBS is loosely attached via the long-range potential, one may think that the nuclear motion associated with the particular vibrational mode excitation of NBS (within the adiabatic picture) is only weakly coupled to anion chemistry and physics. However, the nonadiabatic coupling is prevalent, and NBS dynamics is not an exception. For instance, the vibrationally excited states of DBS located above the electron detachment threshold (Feshbach reso-
nances) are susceptible to the autodetachment process where the excess electron is indirectly liberated by the nonadiabatic coupling of the nuclear motion to the monopole-dipole interaction potential. Although this has long been conceptually accepted as implemented in the Fermi’s golden rule, the mode-specific real-time measurement of the autodetachment rate has not been realized until quite recently by our group. The NBS survives only briefly under some circumstances, and yet it is conceived to play the pivotal role of conveying the electron into the valence orbitals, resulting in real anion chemistry including stable anion formation or immediate chemical bond rupture. Therefore, the final dynamic output should be highly dependent on the nature of the valence orbital where the excess electron is transferred into. The dynamic outputs mediated by the NBS resonances, such as reaction rates and/or product yields, have been probed in a state-specific manner to provide the essential key to disentangling the complicated nonadiabatic dynamics. The competitive dynamics between autodetachment and electron transfer into the valence orbital turns out to be extremely interesting, presenting many challenges in future experimental and theoretical research in the field.

In this Account, we describe the recent advances made in the state-specific chemical dynamics of NBS to provide the unprecedented deep insights into the quantum-mechanical nature of the excess electron in the nonvalence orbital in terms of nonadiabatic coupling into the valence orbitals, as well as the interaction between electronic and nuclear motions beyond the Born–Oppenheimer approximation. Additionally, the dynamic effect of the strong optical field on the excess electron is observed for the first time, and its use for the spatiotemporal manipulation of polyatomic anion systems is envisioned. Notably, our group has introduced the picosecond time-resolved pump–probe spectroscopic technique into the dynamic study of cryogenically cooled anionic species combined with the velocity-map imaging method (Figure 1). The specific vibrational state of NBS could be exclusively selected at a time by the picosecond pump laser pulse ($\Delta t \sim 1.7$ ps, $\Delta E \sim 20$ cm$^{-1}$), and its temporal evolution could be monitored by the pump–probe spectroscopy, facilitating the otherwise formidable task of the state-specific real-time investigation of the NBS dynamics. Detailed experimental methods and analyses have been described in our previous reports.41

## REAL-TIME AUTODETACHMENT DYNAMICS OF THE VIBRATIONAL FESHBACH RESONANCES

As the phenoxyl radical has a large dipole moment of $\sim 4.0$ D, the excess electron is easily bound at the positive end of the dipole. Experimentally, the deprotonated phenol produced in the electrospray ionization (ESI) apparatus was cryogenically cooled in the Paul-type ion trap to generate phenoxide (PhO$^-$) at the internal temperature of $\sim 35$ K (Figure 1). Thereafter, it is optically excited to the DBS with an electron binding energy of $\sim 97$ cm$^{-1}$.42,43 Distinct vibrational Feshbach resonances were identified in the photodetachment spectrum obtained by monitoring the total photoelectron yield as a function of the excitation energy (Figure 2). At the individual vibrational bands, the DBS liberates its excess electron through the autodetachment driven by the wobbling motion of the vibrational mode as manifested in the rather strictly obeyed propensity rule of $\Delta \nu = -1$.42,44,45 The picosecond photoelectron transient of each Feshbach resonant band was obtained.

Figure 2. (a) Picosecond photodetachment spectrum of PhO$^-$ with the DBS state assignments. EA is labeled as the blue arrow. (b) Picosecond photoelectron spectra (left) and time-resolved photoelectron transients (right) at the specific Feshbach resonances. In photoelectron spectra, resonant (black solid line) and nonresonant (blue dashed line) contributions are shown. (c) Schematic diagram of the autodetachment dynamics of the $11^1 18^1$ combinatorial mode. Adapted with permission from ref 1. Copyright 2020 American Physical Society.
obtained by monitoring the low kinetic energy portion of the photoelectron as a function of the temporal delay between the pump and probe laser pulses (Figure 2), revealing the strong mode-dependent autodetachment rate of the DBS. This is the first real-time state-specific measurement of the autodetachment of DBS, providing unprecedented insights into the nonadiabatic coupling of electronic and nuclear motions.

Briefly, the most prominent $11^1$ excitation gives the autodetachment lifetime ($\tau$) of $33.5 \pm 3.0$ ps whereas the excitation of the $18^1$ mode ($+632$ cm$^{-1}$) shows the much shorter lifetime of $5.0 \pm 1.9$ ps. The DBS lifetime of $\tau \approx 11.9 \pm 1.7$ or $9.2 \pm 2.0$ ps found for the $11^2$ ($+1036$ cm$^{-1}$) or $11^3$ mode ($+1556$ cm$^{-1}$), respectively, indicates that the autodetachment is accelerated by the overtone modes. Quite interestingly, the autodetachment is found to be significantly facilitated by the combination mode excitation, giving the extremely short lifetime of $\tau < 1.4$ ps for the $11^1/19^1$ mode.

Fermi’s golden rule for the autodetachment rate ($k$) has been invoked to explain the mode-specific autodetachment rate as follows: 45,46

$$k = \frac{2\pi}{\hbar} |\langle \phi_i | W | \phi_f \rangle|^2 \rho(KE)$$

Here, $\phi_i$ or $\phi_f$ is the initial or final (total) wave function, respectively, whereas $\rho(KE)$ is the density of states of the ejecting electron. The coupling strength ($W$) can be rewritten as follows:

$$\langle \phi_i | W | \phi_f \rangle = - \frac{\hbar^2}{2m} \left( v_f \right) \left( F(Q) \frac{\partial}{\partial Q} \right) \left( v_i \right)$$

$$F(Q) = \frac{1}{\epsilon_{\delta f}} \left( v_{\epsilon f} \left( \frac{\partial U}{\partial Q} \right) \epsilon_i \right)$$

Here, $v_{\epsilon f}$ or $v_{\epsilon i}$ is the vibrational (electronic) wave function of the initial or final state, respectively, whereas $\epsilon_{\delta f}$ is the vibrational energy change upon the autodetachment, and $Q$ is the normal-mode displacement coordinate. For the DBS, because the charge-dipole binding is proportional to the dipole-moment ($\mu$), $\partial U / \partial Q$ should be proportional to $(\partial \mu / \partial Q)$. Therefore, the latter term could be simply estimated from the infrared (IR) intensity which is proportional to $(\partial \mu / \partial Q)^2$. Although the absolute experimental value is hardly reproduced,
the mode-dependent behavior of the autodetachment rate could be rationalized. For instance, according to the Fermi’s golden rule, the $11^{1}$ mode lifetime is predicted to be 2.6 ps if the $11^{1}$ mode lifetime is set to the experimental value of 33.5 ps. This is considerably close to the real experimental value of 5.0 ps found at the $18^{1}$ mode. For the overtone modes of $\Omega_{11}$, as the propensity rule of $\Delta \nu = -1$ is strictly obeyed, the $(\partial \mu/\partial Q)$ term is expected to remain intact for all of $11^{2}$, $11^{3}$, and $11^{4}$ modes. In this case, the derivative Franck–Condon factor of $\left\langle \nu_{i} \left| \frac{\partial}{\partial Q} \right| \nu_{f} \right\rangle$ turns out to be responsible for the increase of the autodetachment rate with the higher overtone mode excitations (Figure 2). Within the harmonic approximation, the autodetachment rate of the $n$th overtone band is expected to be proportional to $n^{2}$, which is in qualitative agreement with the experimental results. As mentioned above, the extraordinarily fast autodetachment of the $11^{4}18^{1}$ combinational mode is quite notable. The autodetachment rate of the two distinct channels of $(\Delta \nu_{11} = -1)$ or $(\Delta \nu_{18} = -1)$ should be $\sim 2.6$ or $\sim 6.7$ times faster than that of the sole $11^{1}$ or $18^{1}$ mode, respectively. This indicates that the two vibrational wobbling motions, when those are combined, may facilitate each other cooperatively as conceptually depicted in Figure 2.

**AUTOODETACHMENT OF DBS, QBS, OR CBS: NATURE OF THE ELECTRON BINDING DYNAMICS**

As the Fermi’s golden rule implies, the autodetachment dynamics of the vibrational resonances is governed by the nature of the electron-neutral interaction potential. Therefore, unlike DBS, the charge-quadrupole interaction potential should be invoked for the QBS. The 4-cyanophenoxide ($4$-ClPhO) anion is a typical QBS system because its unique molecular geometry affords an extremely small dipole moment of $\sim 0.3$ D, whereas it imposes a large quadrupole moment (QM). The spectroscopy of the QBS of 4-CP$^{-}$ has been reported by the Wang group to give an electron binding energy of $\sim 20$ cm$^{-1}$. The autodetachment rate of the QBS, similar to that of the DBS, is found to be dramatically mode-dependent. The dynamic behavior could be well explained by a simple physical model in which the three-dimensional QM ellipsoid is wobbled by nuclear motion. The stereodynamic feature of the nuclear motion with respect to the molecule-fixed angular coordinate is found to be particularly efficient in shaking off the loosely bound electron because the electron-QM tensor potential is very sensitive to the angular position of the electron with respect to the QM ellipsoid. Compared to the case of the DBS or QBS, the proper consideration of the correlation effect on the electron binding dynamics of the NBS (or CBS) is nontrivial. However, it has been considered that the correlation effect may play a significant role in the overall electron binding dynamics even in typical DBS species. Although the theoretical prediction suggests that the correlation effect significantly contributes to the binding energy, insights from the experiment could not be obtained straightforwardly because it is not plausible to sort out the contribution of the correlation effect only from the total binding energy. Incidentally, it has recently been found that the correlation effect may be reflected in the autodetachment dynamics. Namely, the autodetachment of the $11^{1}$ mode of $p$-bromophenoxide ($p$-BrPhO$^{-}$) or $p$-chlorophenoxide ($p$-ClPhO$^{-}$) has been found to be exceptionally slow, giving $r \sim 800$ or 500 ps, respectively (Figure 3). These rates are significantly slow judging from the quantitative comparison with the autodetachment rate of the $11^{1}$ mode of PhO$^{-}$ ($r \sim 33.5$ ps) as that of $p$-BrPhO$^{-}$ or $p$-ClPhO$^{-}$ is expected to be only two times slower than that of PhO$^{-}$ according to the Fermi’s golden rule (vide supra). This inconsistency might come from the correlation effect especially because the strong electron correlation might exist between the excess dipole-bound electron and the electron-rich halogen atomic moiety in $p$-BrPhO$^{-}$ or $p$-ClPhO$^{-}$. Although the correlation effect would be best represented by high-level quantum calculations, we recently modified the charge-dipole interaction potential by invoking the intramolecular electric field. Namely, the effective dipole moment ($\mu_{\text{eff}}$) has been newly defined as the vector sum of the static dipole moment ($\mu_{\text{0}}$) and the induced dipole moment ($\mu_{\text{ind}}$) where the latter is represented by the product of the polarizability tensor ($\partial \mu/\partial Q$) and the intramolecular electric field ($\vec{E}$). This is conceptually consistent with the correlation effect as far as the electron–radical interaction is concerned as the electrons of the neutral core are allowed to be correlated with the excess nonvalence electron by the mediation of the polarizability and the local electric field. Eq 3 can be then modified as follows:

$$F(Q) = \frac{1}{\varepsilon_{0}} \left\langle \varepsilon_{i} \left| \frac{\partial \mu_{\text{eff}}}{\partial Q} \right| \varepsilon_{i} \right\rangle = \frac{1}{\varepsilon_{0}} \left\langle \varepsilon_{i} \left| \left( \frac{\partial \mu_{0}}{\partial Q} + \frac{\partial \mu_{\text{ind}}}{\partial Q} \right) \vec{E} \right| \varepsilon_{i} \right\rangle$$

(4)

Here, the dipole moment change and the polarizability change upon vibrational mode excitation liberate the electron from the DBS. Interestingly, the direction of the dipole moment derivative vector $\left( \frac{\partial \mu_{0}}{\partial Q} \right)$ is opposite to that of the polarizability derivative vector $\left( \frac{\partial \mu_{\text{ind}}}{\partial Q} \right)$ with respect to the $\nu_{11}$ mode for both $p$-BrPhO$^{-}$ and $p$-ClPhO$^{-}$ (Figure 3). This indicates that the effective dipole moment change upon $\nu_{11}$ excitation, due to the cancellation of $\frac{\partial \mu_{0}}{\partial Q}$ and $\frac{\partial \mu_{\text{ind}}}{\partial Q}$ vectors, is diminished resulting in a significantly reduced autodetachment rate. For $p$-BrPhO$^{-}$ or $p$-ClPhO$^{-}$, the correlation effect should thus impede the autodetachment. For PhO$^{-}$, on the other hand, $\left( \frac{\partial \mu_{0}}{\partial Q} \right)$ and $\left( \frac{\partial \mu_{\text{ind}}}{\partial Q} \right)$ share the same direction along the $\nu_{11}$ mode, although the latter is relatively less significant than the former (Figure 3), suggesting that the correlation effect may slightly expedite the autodetachment for the $11^{1}$ mode of PhO$^{-}$. The modified Fermi’s golden rule considering the correlation effect could provide a rational explanation for the experiment. More sophisticated quantum mechanical calculations would be desirable for unraveling the dynamic role of the correlation effect on the autodetachment dynamics of the NBS.

**DOORWAYS INTO THE ANIONIC VALENCE ORBITALS: FRAGMENTATION VERSUS AUTOODETACHMENT**

It has long been conceived that the DBS plays the pivotal role of the doorway to the formation of a stable anion or subsequent chemical reactions. It indicates that the
excess electron in the nonvalence orbital may transform into the valence orbital, and the subsequent chemical reactions in the frame of the anion is destined thereafter depending on the nature of the valence orbital occupied by the excess electron. The doorway role of the DBS has been considered to be important in the formation of interstellar species and the DEA. Whereas the Feshbach resonances of DBS above the electron affinity (EA) are subject to efficient autodetachment (vide supra), those below the EA are most likely to undergo the nonadiabatic transition into the valence-bound state (VBS). This means that the excess electron in the diffuse nonvalence orbital transforms into the nearby valence orbital of the anion. For many DBS species, only the zero-point level (ZPL) of the DBS is identified below EA, although its dynamic behavior has been rarely studied to date. Using picosecond time-resolved spectroscopy, the ZPL of the PhO$^-$ DBS could be clearly isolated, and its real-time dynamics has been investigated for the first time, yielding the lifetime longer than tens of nanoseconds (Figure 4). The long lifetime of the PhO$^-$ DBS at the ZPL is most likely attributed to the slow nonadiabatic transition such as internal conversion into $S_0$. The similar dynamics of the DBS at ZPL could also be found for $p$-BrPhO$^-$ or $p$-CIPhO$^-$, giving $\tau \gg$ ns or $\tau \sim 2$ ns, respectively. For $p$-CIPhO$^-$, the intersystem crossing into the first triplet-state of the anion ($T_1$) may be responsible as it is predicted to be located just below the ZPL of the DBS.

Figure 4. (a) Picosecond time-resolved photoelectron transients of PhO• and para-halogen substituted phenoxides ($p$-XPhO$^-$, X = Cl, Br, and I) obtained at DBS ZPL. Transients were fitted by a single-exponential decay function, while transients for $p$-CIPhO$^-$ and $p$-BrPhO$^-$ were fitted by two-single exponential decay function with opposite signs. (b) Calculated energetic diagrams of the $p$-CIPhO$^-$, $p$-BrPhO$^-$, and $p$-PhO$^-$ calculated by the TD-DFT calculations. The HOMO and LUMO of $p$-PhO$^-$ were depicted in the inset. (c) Potential energy curves of the $S_0$ (black), $T_1$ (purple), $S_1$ (yellow), and $D_0$ (red) of the $p$-IPhO$^-$ along the C–I bond extension coordinate based on the TD-DFT calculation (B3LYP/Def2TZVP). The vertical excitation from the optimized geometry of the anionic ground state to the DBS (or $D_0$) is denoted as the blue arrow. Adapted with permission from ref 53. Copyright 2021 American Chemical Society.
with respect to the EA. And yet, it is found that the relative yields of the photoelectron (ejected from the autodetachment) and I$^-$ fragment (resulting from the DBS-VBS ($S_1$) transition) vary among different vibrational modes, giving entirely different spectral patterns for the photodetachment and fragment-action spectra. Because the autodetachment is blocked, the fragmentation should be the dominant channel at the ZPL, giving the significantly pronounced peak in the I$^-$ fragment action spectrum at the ZPL. At DBS resonances above the EA, the autodetachment and fragmentation compete with each other. This indicates that the relative yields of the photoelectron and I$^-$ fragment should be determined by the relative speeds of these two distinct processes, opening a new way for controlling the reaction, possibly through the manipulation of the quantum-mechanical nature of the DBS doorway state.

Actually, as the vibrational autodetachment rate is strongly mode-dependent (vide supra) in the wide dynamic range, the competing dynamics between autodetachment and fragmentation could be well explained. For instance, if there is only one decaying channel of autodetachment, the 11$^1$ mode is supposed to be more pronounced than the 10$^1$ mode (regardless of their relative lifetimes) in the photodetachment spectrum according to the Franck–Condon prediction. The experiment is, however, completely different from the Franck–Condon prediction, showing that the 11$^1$ band is only weakly observed whereas the 10$^1$ mode is significantly pronounced (Figure 5). The mode-dependent behavior of the I$^-$ fragment yield is found to be completely opposite to that of the photoelectron yield. Namely, the I$^-$ fragment yield stands out at the 11$^1$ mode while it is much reduced at the 10$^1$ mode. This should be attributed to the fact that the autodetachment rate of the 10$^1$ mode is much faster than that of the 11$^1$ mode, mainly due to the stronger IR intensity of the former, affording a relatively larger autodetachment yield for 10$^1$ compared to 11$^1$. That is, the autodetachment prevails in the kinetic competition with the DBS-VBS transition at the 10$^1$ mode, while it is completely the other way around at the 11$^1$ mode where the rapid fragmentation channel becomes dominant. It should be emphasized that both autodetachment and fragmentation most significantly occur only through the DBS resonances, confirming the long-standing premise that the DBS plays the role of the doorway to the anion formation and subsequent chemical reactions such as DEA.

The situation becomes somewhat different for the o-iodophenoxide (o-IPhO$^-$), Figure 5. Here, the I$^-$ fragment yield is resonantly enhanced very strongly only at the ZPL, whereas it is substantially diminished at all additional DBS resonances above the EA. This indicates that the fragmentation occurs predominantly only when the autodetachment is blocked. For the DBS resonances above EA, the fast autodetachment process becomes dominant, and thus, the relatively slower DBS to VBS transition is significantly suppressed. Actually, the lifetime of the DBS o-IPhO$^-$ at the
ZPL has been measured to be \( \sim 724 \text{ ps} \), which is considerably longer than the DBS (ZPL) lifetime of \( \sim 9.5 \text{ ps} \) of \( p^{-}\text{IPhO}^{-} \) (vide supra). This experimental fact perfectly conforms to the mode-dependent dynamic behavior of autodetachment and fragmentation. That is, as the DBS to VBS transition rate is slowed in \( o^{-}\text{IPhO}^{-} \), the relatively much faster autodetachment (\( \tau \sim 12.3 \text{ ps} \) for the \( C^{-}\text{O} \) in-plane stretching \( 18^{1} \) mode, for instance) becomes dominant for most vibrational resonances above the EA, giving the photodetachment spectrum with well-pronounced resonant DBS bands consistent with the Franck-Condon prediction. The rather slow DBS to VBS (\( S_{1} \)) transition of \( o^{-}\text{IPhO}^{-} \) at the ZPL may be due to the significantly large barrier along the \( C^{-}\text{I} \) bond extension coordinate (Figure S).

\section{PONDEROMOTIVE EFFECT ON THE QUASI-FREE ELECTRON OF THE NBS}

The atomic Rydberg state in a strong optical field has long been intensively investigated for high-harmonic generation and atomic-lattice manipulation in a quantum-simulator.\textsuperscript{54–56} However, for polyatomic molecular systems, because of the highly probable penetration of the Rydberg electron into the molecular core, intact manipulation by a strong optical field has been challenging. We recently found that the DBS resonances show the AC-Stark shifts in a strong optical field. This is the first observation of a ponderomotive effect on the DBS. The entire vibrational resonant states of the PhO\(^{-}\) DBS are found to be blue-shifted in the presence of the spatiotemporally overlapped control laser pulse (Figure 6), providing the clear evidence for the ponderomotive force exerted on the quasi-free electron of the DBS.

The AC-Stark shift is expected to be proportional to the intensity of the control laser pulse according to the relation among the ponderomotive potential \( (U_{p}) \), polarizability of the electron \( (\alpha_{e}) \), and laser intensity \( (E^{2}) \) as follows:

\[
U_{p} = -\frac{1}{4}\alpha_{e}E^{2}(t) \tag{5}
\]

Indeed, the (blue) spectral shift of the \( 11^{1} \) DBS band of PhO\(^{-}\) increases linearly with the increase in the intensity of the control laser pulse (Figure 6). The slope of this plot represents the polarizability of the electron. In general, \( \alpha_{e} \) has a maximum value for the free-electron, whereas it decreases as the electron becomes more strongly bound. As expected, the slope of the Stark shift with increasing the control laser intensity for PhO\(^{-}\) is smaller than that of the free-electron model as expected.
Quite intriguingly, the slope of the ponderomotive shift versus the laser intensity is found to be considerably steeper in the QBS of 4-CP than that of PhO\textsuperscript{−}, indicating that the quasi-free electron of the QBS may be more polarizable than that of the DBS. Notably, the electron polarizability is seemingly not sensitive to the electron binding energy as the ponderomotive shift observed for 4-BrPhO of which the electron binding energy of DBS is very small (~20 cm\textsuperscript{-1})\textsuperscript{36} shows the almost identical behavior to that of PhO\textsuperscript{−} despite that the electron binding energy of the latter is significantly larger (~97 cm\textsuperscript{-1})\textsuperscript{32,43} Therefore, the polarizability of the quasi-free electron seemingly originates from the nature of the electron-neutral interaction potential. Namely, the nonvalence electron of QBS behaves more like a free electron compared to that of DBS, indicating that the nonvalence orbital of QBS is more diffuse and polarizable in the external oscillating electromagnetic field compared to that of DBS. The experimental observation of the ponderomotive effect on the excess electron in the DBS (or QBS) may be utilized as a novel tool to manipulate the dynamic behavior of the polyatomic molecular systems not only in terms of spatial manipulation but also in the control of chemical reactions.

**CONCLUSIONS AND OUTLOOK**

In this Account, we have described how the excess electron residing in the diffuse nonvalence orbital behaves in terms of liberation by vibrational wobbling (autodetachment) or transformation into the valence orbital to either generate a stable anion or induce chemical-bond fragmentation. State-specific chemical dynamics revealed by a series of picosecond time-resolved pump–probe spectroscopic studies provides the solid platform for understanding the dynamic role of the metastable NBS resonances. The new perspective for the anionic reaction control is given as both the autodetachment and NBS–VBS transition rates of the excess electron are strongly mode-dependent. The observation of the ponderomotive force exerted on the nonvalence orbital in the strong optical field may lead to the spatiotemporal manipulation of the molecular anions as well as the AC-Stark control of the chemical reaction. As the NBS plays the role of a doorway to anion chemistry, it may be used to open or close the door in terms of the probability through unique quantum-mechanical resonant windows. Femtosecond or attosecond time-resolved spectroscopic techniques might allow real-time snapshots of the electron movement from the nonvalence to valence orbitals (or *vice versa*) associated with the particular nuclear motions.\textsuperscript{30,39} The study of the solvation effect on the NBS dynamics of the well-designed cluster system would also be quite valuable, as it would help to understand the fundamentals regarding the anion reactions in the bulk medium.\textsuperscript{30,57} There are many experimental and theoretical challenges remaining in the field of anion chemistry and physics, and it is hoped that the state-specific NBS dynamics briefly described here would serve as a cornerstone for extremely interesting studies in the coming years.

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**Notes**

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