

Effect of Incremental Hydration on Reverse Internal Conversion Vibrational Autodetachment of an Anion

E. Michi Burrow¹, Connor J. Clarke¹, and Jan R. R. Verlet^{1,2,*}

¹*Department of Chemistry, Durham University, Durham DH1 3LE, United Kingdom*

²*J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Dolejškova 3, 18223 Prague 8, Czech Republic*



(Received 22 April 2025; accepted 4 August 2025; published 3 September 2025)

The recently discovered mechanism of reverse internal conversion vibrational autodetachment (RICVAD), by which an excess electron is emitted at specific energies from an isolated hot ground state anion, is mediated by the statistical population of a dipole-bound state. Here, we consider how this process is influenced by the presence of up to two water molecules. Using anion photoelectron imaging of the nitrobenzene radical anion, NB^- , clustered to water molecules, we find that RICVAD remains active for $\text{NB}^-(\text{H}_2\text{O})_1$. However, we also find that an additional decay channel opens at higher photoexcitation energies, which arises from dissociation of the cluster upon accessing an electronic resonance of $\text{NB}^-(\text{H}_2\text{O})_1$, forming hot isolated NB^- , which then undergoes RICVAD. $\text{NB}^-(\text{H}_2\text{O})_2$ also shows evidence of RICVAD, but its signatures are obscured by other low energy electron signal. Our work shows that the RICVAD mechanism remains possible in a complex environment and shows how resonance dynamics are influenced by hydration.

DOI: 10.1103/zfxx-8r4x

Nonvalence states of anions have been topical because of their role in electron attachment [1–8] and detachment [9–11], and in photodynamical processes [12–17]. Recently, a new electron emission mechanism involving nonvalence states, coined reverse internal conversion vibrational autodetachment (RICVAD), has been observed for anions [18,19], which has analogies to recurrent fluorescence [20,21] and thermally activated delayed fluorescence [22], in which light is emitted following reverse internal conversion instead of electrons. In RICVAD, hot ground state anions that would normally undergo thermionic emission can statistically populate a nonvalence state of the anion near the threshold of electron detachment, from which an electron is then emitted by mode-specific vibrational autodetachment (VAD) [18,19]. The thermal population of the nonvalence state takes place on a nano- to millisecond timescale, while VAD of the nonvalence state once formed typically proceeds on a picosecond timescale [10,13–16,23,24]. RICVAD has been observed and characterized for the nitrobenzene radical anion NB^- , following either photon or electron excitation [18,19], where the mediating nonvalence state is a dipole-bound state [25,26]. There has also been significant interest in the influence of local environment on nonvalence states of

anions, and in particular, in understanding how nonvalence states behave in the presence of solvent molecules [27–30]. This leads to the natural question: how will solvent molecules affect RICVAD? Here, we address this question for NB^- in the presence of a few water molecules, $\text{NB}^-(\text{H}_2\text{O})_n$.

In an electron emission spectrum, the spectral signatures of RICVAD are distinct peaks at low electron kinetic energy that can be correlated with VAD, along with the typical Boltzmann distribution arising from competing thermionic emission. The process has been experimentally observed through two complementary methods: 2D electron energy loss spectroscopy [31–35], $\text{NB} + e_i^- \rightarrow \text{NB}^{*-} \rightarrow \text{NB} + e_f^-$, where e_i^- is the incoming electron (with kinetic energy ε_i), NB^{*-} is an intermediate excited state of the NB anion lying in the detachment continuum (i.e., an electronic resonance), and e_f^- is the outgoing electron; and 2D anion photoelectron spectroscopy [36–40], $\text{NB}^- + h\nu \rightarrow \text{NB}^{*-} \rightarrow \text{NB} + e_f^-$ [18,19]. The incoming energy can be scanned across the continuum by either varying ε_i or $h\nu$ (where $h\nu$ is greater than the adiabatic electron affinity of NB) and, in both cases, the kinetic energy of e_f^- , ε_f , is measured and contains information about the RICVAD process, along with more direct scattering processes. For NB^- , RICVAD was observed as a distinct peak at $\varepsilon_f = 0.06$ eV, with some additional mode-specific features, on top of a thermionic emission background signal. It allowed an onset for the RICVAD to be determined in both experiments, highlighting the role of NB^{*-} as an intermediate, where NB^{*-} is transiently populated (either by electron excitation or photon excitation) and internally converts to reform the NB^- ground electronic state with high internal energy that cannot be

*Contact author: j.r.r.verlet@durham.ac.uk

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International license](#). Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

dissipated in the isolated system. We now extend this to explore the role of a solvent molecule, H_2O , on the dynamics of NB^{*-} and the subsequent RICVAD process. We chose water as the most ubiquitous solvent and because it is a strongly interacting solvent, which may be anticipated to lead to the greatest perturbation on the RICVAD mechanism. Probing incremental solvation in electron energy loss spectroscopy is challenging because of the difficulty in mass selection of the target cluster, $\text{NB}(\text{H}_2\text{O})_n$ [41,42]. In contrast, for anion 2D photoelectron spectroscopy, the target is charged and mass selection of $\text{NB}^-(\text{H}_2\text{O})_n$ prior to the experiment is straightforward [43–45], and we therefore resort to this latter method.

The experimental set up has been described in detail previously [46]. Briefly, a backing gas of argon at 10 bar was seeded with NB and water vapor at room temperature and expanded into high vacuum using a pulsed Even-Lavie valve [47]. The resulting supersonic expansion passed through a ring filament ionizer to generate $\text{NB}^-(\text{H}_2\text{O})_n$. Anions were mass selected using a time-of-flight mass spectrometer [48] and intersected with the output of an Nd:YAG-pumped optical parametric oscillator (OPO). Generated photoelectrons were collected using a velocity-map imaging [49] photoelectron spectrometer. Photoelectron spectra were generated from raw images using the polar onion peeling algorithm [50] and were calibrated using the electron affinity of NB, $EA = 0.98$ eV, and vibrational frequencies of neutral NB [51,52]. The spectrometer has a resolution of $\sim 3\%$ of ϵ_f . Quantum chemical calculations were performed on NB and $\text{NB}(\text{H}_2\text{O})_1$ at the MP2/aug-cc-pVDZ level of theory using Gaussian16 [53–55] to determine the geometries and vibrational frequencies. Computed spectra are available in the supporting information [56].

Figure 1 shows the 2D photoelectron spectra of $\text{NB}^-(\text{H}_2\text{O})_n$ for $n = 0$ and 1, taken at $h\nu$ intervals of 0.1 eV. The 2D photoelectron spectrum of $\text{NB}^-(\text{H}_2\text{O})_0$, remeasured here and shown in Fig. 1(a) and with the $h\nu = 1.8$ eV spectrum omitted because of poor signal level (near degeneracy of the OPO), has been analyzed in detail previously [18,19]. Briefly, the key features are the diagonal signals that arise from direct detachment from NB^- into the continuum: $\text{NB}^- + h\nu \rightarrow \text{NB} + e_f^-$, and the onset at $h\nu \approx 1.7$ eV of a RICVAD feature that peaks at $\epsilon_f = 0.06$ eV (see Supplemental Material [56]). The direct detachment feature has several resolved peaks that arise from Franck-Condon factors in direct detachment, $\text{NB}^- + h\nu \rightarrow \text{NB} + e_f^-$ (predominantly the NO_2 symmetric stretch in NB). Stark changes in Franck-Condon factors are apparent for photon energies above $h\nu > 2.4$ eV, which come about from excitation to electronic resonances, NB^{*-} [18,19,57,58]. However, excitation does not necessarily lead to observable changes in Franck-Condon factors, and excitation to other resonances also occurs between $1.7 < h\nu < 2.4$ eV, and at higher $h\nu$, as evidenced by the large range over which RICVAD is observed [18,19].

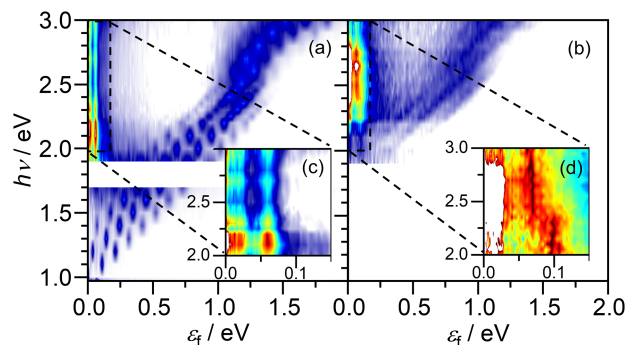


FIG. 1. 2D photoelectron spectra of NB^- (a) and $\text{NB}^-(\text{H}_2\text{O})_1$ (b), with the low kinetic energy (ϵ_f) regions enlarged (c) and (d). Some signal has been saturated in (d) to highlight the change in ϵ_f of the RICVAD signal with excitation energy, $h\nu$.

Figure 1(b) shows the 2D photoelectron spectrum of $\text{NB}^-(\text{H}_2\text{O})_1$, which highlights some similarities and differences between this complex and the bare anion. A diagonal feature is also seen with a similar Franck-Condon profile, arising from the direct detachment process $\text{NB}^-(\text{H}_2\text{O})_1 + h\nu \rightarrow \text{NB}(\text{H}_2\text{O})_1 + e_f^-$. The onset of the diagonal feature appearing at higher energy can be rationalized by the larger binding energy between the NB^- with H_2O compared to that of NB with H_2O , which needs to be overcome to reach the neutral surfaces [59–61]. In the present case, the increase in electron affinity is 0.52 eV. The changes in the Franck-Condon profile seen for NB^- are also seen in $\text{NB}^-(\text{H}_2\text{O})_1$, suggesting that the same NB^{*-} resonance is available in the cluster, although the onset is slightly higher in excitation energy ($h\nu \sim 2.6$ eV compared to ~ 2.4 eV in NB^-). The observed solvatochromatic shift is consistent with UV-vis spectra of NB^- in solution, which show that the absorption maximum blueshifts in the presence of water [62].

Finally, a low kinetic energy feature that appears commensurate with RICVAD can also be seen for $\text{NB}^-(\text{H}_2\text{O})_1$ across the entire measured energy range. The onset of the RICVAD feature is difficult to ascertain, as it is close to the onset of the vertical direct detachment, but it is broadly consistent with that seen for NB^- . Hence, RICVAD appears to be operable in the cluster. However, closer inspection of the RICVAD (low kinetic energy) feature, as magnified in Fig. 1(d), indicates that the feature changes with $h\nu$, peaking initially around $\epsilon_f \sim 0.10$ eV for $h\nu < 2.4$ eV and shifting to $\epsilon_f \sim 0.06$ eV for $h\nu > 2.5$ eV.

Figure 2(b) shows photoelectron spectra of the low-energy RICVAD region for $h\nu = 2.2$ eV and 2.8 eV that are representative of the two distinct RICVAD features observed in $\text{NB}^-(\text{H}_2\text{O})_1$. Also included in Fig. 2(a) is a photoelectron spectrum of NB^- taken at $h\nu = 2.8$ eV for comparison, which is representative of its entire $h\nu$ range [Fig. 1(c)]. The RICVAD feature in $\text{NB}^-(\text{H}_2\text{O})_1$ observed at $\epsilon_f \sim 0.06$ eV aligns very well with that observed for NB^- , suggesting that this feature arises from the bare anion

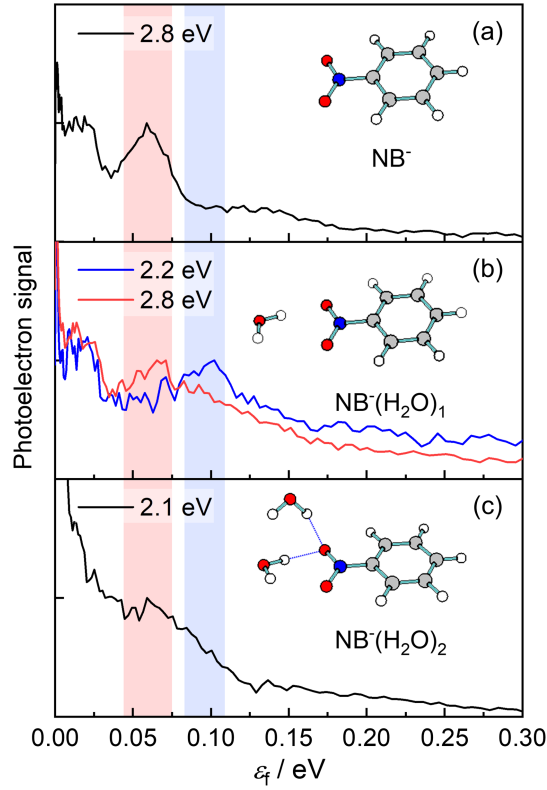


FIG. 2. Photoelectron spectra with RICVAD features for NB^- (a), $\text{NB}^-(\text{H}_2\text{O})_1$ (b), and $\text{NB}^-(\text{H}_2\text{O})_2$ (c). For $\text{NB}^-(\text{H}_2\text{O})_1$, two photon energies are shown to indicate the differing contributions to the RICVAD signals, which are highlighted by shaded regions.

(i.e., water has been lost *prior* to RICVAD). This is the dominant channel for $h\nu > 2.5$ eV. At lower $h\nu$, the RICVAD feature appears blueshifted to $\epsilon_f \sim 0.10$ eV and does not align with features from NB^- , suggesting it arises from RICVAD of the cluster, $\text{NB}^-(\text{H}_2\text{O})_1$.

Before we consider the origin of the apparent switch in processes from RICVAD *before* H_2O loss at low $h\nu$ to RICVAD *after* H_2O loss at high $h\nu$, we first consider the spectral appearance of RICVAD from $\text{NB}^-(\text{H}_2\text{O})_1$. The RICVAD feature for bare NB^- has previously been explained by the involvement of specific vibrational modes that lead to electron emission from the dipole-bound state of NB^- [18,19]. Because the potential energy surface of the nonvalence and neutral states are very similar, vibrational autodetachment has a $\Delta v = -1$ propensity rule [18,63–67] that leads to VAD with energies $\epsilon_f = \epsilon_{\text{vib}} - \epsilon_{\text{NVS}}$, where ϵ_{vib} is the energy of the mediating vibrational mode and ϵ_{NVS} is the electron binding energy of the nonvalence state. For NB^- , $\epsilon_{\text{NVS}} = 27$ meV [18,68]. The vibrational modes that are predominantly involved are those that strongly modulate the dipole moment of the neutral (i.e., the IR-active modes). For NB, the b_1 , ν_{20} out-of-plane symmetric hydrogen stretching mode correlates with the $\epsilon_f = 0.06$ eV feature, with symmetric (a_1 , ν_6) and asymmetric (b_2 , ν_{28}) NO_2 stretches contributing at higher ϵ_f [18]. The

computed IR spectrum of $\text{NB}(\text{H}_2\text{O})_1$ is similar to NB (see Supplemental Material [56]), hence the shift in ϵ_f may be due to a difference in ϵ_{NVS} . However, calculations indicate that the overall dipole moment of $\text{NB}(\text{H}_2\text{O})_1$ is larger than that of NB, suggesting that ϵ_f for RICVAD involving the same modes would redshift in the cluster, in contrast to the observed blueshift. Instead, the higher-lying ν_6 and ν_{28} modes can also contribute. Specifically, ν_6 , has a calculated vibrational frequency of 1400 cm^{-1} (174 meV), for which $\epsilon_f = \epsilon_{\text{vib}} - \epsilon_{\text{NVS}}$ would likely contribute to the observed peak at $\epsilon_f \sim 0.10$ eV. Based on this assignment, we estimate $\epsilon_{\text{NVS}} \sim 174\text{ meV} - 100\text{ meV} = 74\text{ meV}$; an increase of about 47 meV compared to the bare NB molecule. Although ν_6 is highly IR active [18], it is likely weak in the NB^- RICVAD spectrum, because the RICVAD yield is expected to scale similarly to thermionic emission (which becomes exponentially weaker at higher ϵ_f). As it moves to lower energy on account of higher ϵ_{NVS} , the ν_6 mode is likely to gain intensity in the RICVAD signal, consistent with the observations.

Regardless of the exact details of the modes involved in RICVAD, it is clear that RICVAD is operable in $\text{NB}^-(\text{H}_2\text{O})_1$, which is in itself striking given the additional degrees of freedom. However, from Fig. 1(d), it is only observed for $h\nu < 2.4$ eV. So why does the RICVAD from $\text{NB}^-(\text{H}_2\text{O})_1$ change to RICVAD from NB^- around $h\nu \sim 2.5$ eV? Figure 3 shows the percentage yield of electrons at $\epsilon_f \sim 0.06$ eV and at $\epsilon_f \sim 0.10$ eV, estimated by fitting the RICVAD signal using two Gaussian functions of varying amplitudes at different $h\nu$ (see [56]).

For RICVAD to occur from NB^- following excitation of $\text{NB}^-(\text{H}_2\text{O})_1$, the H_2O molecule must have dissociated from the cluster prior to electron loss. This could occur through a statistical process, much like RICVAD. However, we do not consider this to be viable. First, competition between statistical evaporation or electron emission from the ground state will generally favor the process with lowest activation energy at lower temperatures (photon energies). In the current case, this would suggest that evaporation would dominate at low $h\nu$. Moreover, the prevalence of both processes should equalize as $h\nu \rightarrow \infty$. Finally, the change in observed processes takes place over a relatively small energy range (<1 eV), which is inconsistent with a statistical process. Hence, it appears that the primary step must involve H_2O loss from excited states, $[\text{NB}^-(\text{H}_2\text{O})_1]^*$.

The resonances of NB^- have been characterized by electron transmission and electron energy loss spectroscopy, as well as by computational methods [18,19,57,69]. Two π^* shape resonances have been identified at $\epsilon_1 \sim 0.5$ and 1.3 eV, which correspond to the $^2A_2$ and $^2B_1$ resonances, respectively (C_{2v} symmetry). The $^2A_2$ state is optically dark and instead, the onset of the RICVAD observed for NB^- has been correlated to excitation to the $^2B_2$ Feshbach resonance located at $\epsilon_1 \sim 0.72$ eV ($h\nu \sim 1.7$ eV), which has a broad Franck-Condon profile (and is dark in electron transmission

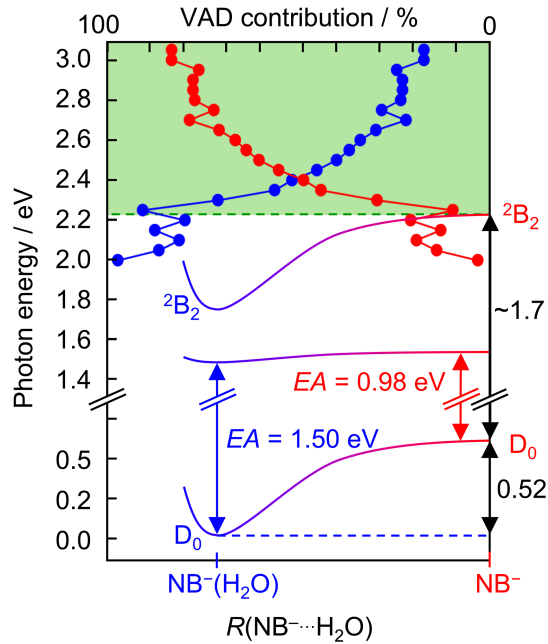


FIG. 3. Positions of the D_0 and ${}^2B_2$ states in NB^- and $\text{NB}^-(\text{H}_2\text{O})_1$, and the S_0 neutral ground states in each, overlaid with the relative intensity of VAD from each species at fixed photon energies. Blue circles denote VAD originating from $\text{NB}^-(\text{H}_2\text{O})_1$ and red from NB^- .

spectroscopy). The ${}^2B_1$ shape resonance on the other hand is bright and has an onset of $h\nu \sim 2.4$ eV and its impact on the 2D photoelectron spectrum can be clearly seen for NB^- in Fig. 1(a) and for $\text{NB}^-(\text{H}_2\text{O})_1$ in Fig. 1(b). At first glance, excitation to the ${}^2B_1$ shape resonance can be roughly correlated with the switchover observed in Fig. 3, suggesting that this resonance might be mediating water loss. However, unless this resonance is highly dissociative to H_2O loss, the timescale of dissociation would far exceed the autodetachment timescale, which—for a shape resonance—is expected to be subpicosecond [70,71]. Furthermore, the onset of the evaporation channel in Fig. 3 is ~ 0.4 eV below the onset of the ${}^2B_1$ resonance in Fig. 1(b). Hence, the ${}^2B_1$ resonance does not appear to be responsible for the water dissociation pathway.

The ${}^2B_2$ Feshbach resonance is also located in the vicinity of the observed switchover of RICVAD mechanisms. Its onset in the 2D photoelectron spectrum [Fig. 1(b)] is unclear, in part because it is expected to be broad (as in NB^-), and because it is close to the electron affinity of the cluster. To consider whether the ${}^2B_2$ Feshbach resonance may be the origin of the observed water-loss channel, we consider the energetics involved. Specifically, Fig. 3 shows sketches of potential energy surfaces of the ground state and the ${}^2B_2$ resonance of $\text{NB}^-(\text{H}_2\text{O})_1$, along the $\text{NB}^- \cdots \text{H}_2\text{O}$ coordinate, $R(\text{NB}^- \cdots \text{H}_2\text{O})$.

The onset of the ${}^2B_2$ resonance of NB^- is known to take place at $h\nu \sim 1.7$ eV from previous work [18], as indicated

in Fig. 3. The energy difference between the $\text{NB}^-(\text{H}_2\text{O})_1$ ground state and its dissociated pair $\text{NB}^- + \text{H}_2\text{O}$ is ~ 0.52 eV from the increase in the electron affinity upon solvation (if we neglect the comparatively small binding energy between neutral NB and H_2O). Hence, the excitation energy from the initial $\text{NB}^-(\text{H}_2\text{O})_1$ ground state required to reach the dissociation limit of the ${}^2B_2$ resonance to form $\text{NB}^- + \text{H}_2\text{O}$ is approximately the sum of these two energies, which amounts to $h\nu \sim 2.2$ eV, shown with the green dashed line in Fig. 3. This aligns with the $h\nu$ at which RICVAD channels begin to change (Fig. 3) and suggests that, once exceeded, a water molecule can leave from the ${}^2B_2$ resonance in $\text{NB}^-(\text{H}_2\text{O})_1$. This would require water loss to be fast relative to autodetachment, which may be the case given that the ${}^2B_2$ resonance is of Feshbach character, requiring an electronic transition alongside autodetachment, leading to a typical autodetachment lifetime of a few picoseconds. Note also that the ${}^2B_2$ resonance corresponds to the first $n\pi^*$ state of $\text{NB}^-(\text{H}_2\text{O})_1$, where the electron density shifts away from the $-\text{NO}_2$ group and toward the π system, likely weakening the binding of the in-plane water molecule [see Fig. 2(b)] and potentially facilitating water loss. The dynamic water loss from the ${}^2B_2$ resonance prior to autodetachment is analogous to the dissociative electron attachment mechanism: $\text{NB}(\text{H}_2\text{O})_1 + e^- \rightarrow \text{NB}^- + \text{H}_2\text{O}$.

2D photoelectron spectroscopy was also performed for $\text{NB}^-(\text{H}_2\text{O})_2$. A representative RICVAD spectrum is shown in Fig. 2(c). Evidence for RICVAD can be seen at low ϵ_f , with some apparent structure on top of the thermionic emission distribution. However, it is difficult to distinguish, and the features have large spectral breadth, such that no meaningful frequencies can be extracted. This either means that the RICVAD mechanism is only sparingly operable in the larger cluster, or it might be that the RICVAD signatures have been broadened so much that it is mostly indistinguishable from thermionic emission. Indeed, comparing the spectral profile of RICVAD from NB^- and $\text{NB}^-(\text{H}_2\text{O})_1$ in Figs. 2(a) and 2(b) suggests that there is spectral broadening of the RICVAD feature in the presence of a water molecule. This would of course not be surprising as the ground electronic state anion that is formed *en route* to RICVAD has high internal energy so that the water molecule is likely to be quite dynamic around the NB^- core on the timescale of the RICVAD (which is likely to be many nanoseconds if not microseconds). Furthermore, water molecules have been reported to be mobile in other systems, particularly those of high symmetry, even within a cold molecular beam [72,73]. The consequence of a dynamic water molecule is that there will be a distribution of dipole moments and therefore a distribution of binding energies of the dipole-bound state [30], $\Delta\epsilon_{\text{NVS}}$, which ultimately leads to a distribution of final RICVAD energies: $\Delta\epsilon_f = \epsilon_{\text{vib}} - \Delta\epsilon_{\text{NVS}}$.

Nevertheless, the only hint of a peak for $\text{NB}^-(\text{H}_2\text{O})_2$ aligns well with RICVAD from NB^- , possibly suggesting

that both water molecules might have been lost. However, we caution such a conclusion because of the many additional complexities. First, higher-frequency VAD-active modes may have redshifted further compared to $n = 1$ on account of an increased ϵ_{NVS} (e.g., an additional 40 meV, consistent with the 47 meV from the first H_2O). Second, water loss dynamics could be occurring at different energies (note that NB^- exhibits solvatochromaticity [62]) and there could be new dynamical processes taking place. Finally, if H_2O dissociation is competing, then there are potentially three competing RICVAD channels ($n = 2, 1$, and 0).

In conclusion, we have observed that the recently discovered RICVAD mechanism by which nonvalence states are statistically populated leading to mode-specific VAD persists in the presence of a few water molecules. For solvation by a single water molecule, we can identify the dominant mode leading to VAD. We have also observed stark changes in the dynamics taking place following initial excitation to electron impact resonances. Specifically, for $h\nu < 2.5$ eV, RICVAD is observed from $\text{NB}^-(\text{H}_2\text{O})_1$ while for $h\nu \gtrsim 2.5$ eV, RICVAD is observed from NB^- , which necessitates the loss of the H_2O molecule prior to electron loss. We assign this to the excitation of a Feshbach resonance, which becomes dissociative along the $\text{NB}^- \cdots \text{H}_2\text{O}$ coordinate when its binding energy is exceeded. The observation of energy dependent dynamics, imposed by the added complexity of the solvent molecule, highlights the rich chemical physics that can take place in the detachment continuum and poses a challenge to computational chemistry. The observation of RICVAD in clusters opens a new mechanism in clusters that was hitherto unknown.

Supplementary Material is available [56], showing additional photoelectron spectra that support the findings in this work, the *ab initio* calculations that assisted in the vibrational assignments of the RICVAD signal, and the data fitting that showed the relative intensities of the RICVAD signal in spectra taken at different photon energies.

Acknowledgments—This work was funded by the EPSRC under Grant No. EP/V007971/1 (E. M. B., J. R. R. V.), the OP JAK Project No. CZ.02.01.01/00/22_008/0004649 (QUEENTEC) (J. R. R. V.), and Durham University for a Scholarship (C. J. C.).

Data availability—The data that support the findings of this Letter are openly available [74].

- [1] T. Sommerfeld, Dipole-bound states as doorways in (dissociative) electron attachment, *J. Phys. Conf. Ser.* **4**, 245 (2005).
- [2] C. Desfr  ois, H. Abdoul-Carime, N. Khelifa, and J. P. Schermann, From $1/r$ to $1/r^2$ potentials: Electron exchange between Rydberg atoms and polar molecules, *Phys. Rev. Lett.* **73**, 2436 (1994).

- [3] R. D. Mead, K. R. Lykke, W. C. Lineberger, J. Marks, and J. I. Brauman, Spectroscopy and dynamics of the dipole-bound state of acetaldehyde enolate, *J. Chem. Phys.* **81**, 4883 (1984).
- [4] P. J. Sarre, The diffuse interstellar bands: A dipole-bound state hypothesis, *Mon. Not. R. Astron. Soc.* **313**, L14 (2000).
- [5] C. E. H. Dessent, J. Kim, and M. A. Johnson, Spectroscopic observation of vibrational Feshbach resonances in near-threshold photoexcitation of $\text{X}^- \cdot \text{CH}_3\text{NO}_2$ ($\text{X}^- = \text{I}^-$ and Br^-), *Faraday Discuss.* **115**, 395 (2000).
- [6] A. Kunin and D. M. Neumark, Time-resolved radiation chemistry: Femtosecond photoelectron spectroscopy of electron attachment and photodissociation dynamics in iodide–nucleobase clusters, *Phys. Chem. Chem. Phys.* **21**, 7239 (2019).
- [7] J. P. Rogers, C. S. Anst  ter, and J. R. R. Verlet, Evidence of electron capture of an outgoing photoelectron wave by a nonvalence state in $(\text{C}_6\text{F}_6)_n^-$, *J. Phys. Chem. Lett.* **9**, 2504 (2018).
- [8] J. P. Rogers, C. S. Anst  ter, and J. R. R. Verlet, Ultrafast dynamics of low-energy electron attachment via a nonvalence correlation-bound state, *Nat. Chem.* **10**, 341 (2018).
- [9] G.-Z. Zhu and L.-S. Wang, High-resolution photoelectron imaging and resonant photoelectron spectroscopy via non-covalently bound excited states of cryogenically cooled anions, *Chem. Sci.* **10**, 9409 (2019).
- [10] J. N. Bull, C. W. West, and J. R. R. Verlet, Ultrafast dynamics of formation and autodetachment of a dipole-bound state in an open-shell π -stacked dimer anion, *Chem. Sci.* **7**, 5352 (2016).
- [11] T.-C. Jagau, D. B. Dao, N. S. Holtgrewe, A. I. Krylov, and R. Mabbs, Same but Different: Dipole-Stabilized Shape Resonances in CuF^- and AgF^- , *J. Phys. Chem. Lett.* **6**, 2786 (2015).
- [12] C. Desfr  ois, H. Abdoul-Carime, and J.-P. Schermann, Ground-state dipole-bound anions, *Int. J. Mod. Phys. B* **10**, 1339 (1996).
- [13] J. N. Bull, C. S. Anst  ter, and J. R. R. Verlet, Ultrafast valence to nonvalence excited state dynamics in a common anionic chromophore, *Nat. Commun.* **10**, 5820 (2019).
- [14] C. J. Clarke and J. R. R. Verlet, Dynamics of anions: From bound to unbound states and everything in between, *Annu. Rev. Phys. Chem.* **75**, 89 (2024).
- [15] D. H. Kang, J. Kim, H. J. Eun, and S. K. Kim, State-specific chemical dynamics of the nonvalence bound state of the molecular anions, *Acc. Chem. Res.* **55**, 3032 (2022).
- [16] J. R. R. Verlet, C. S. Anst  ter, J. N. Bull, and J. P. Rogers, Role of nonvalence states in the ultrafast dynamics of isolated anions, *J. Phys. Chem. A* **124**, 3507 (2020).
- [17] D. H. Kang and S. K. Kim, Reaction dynamics of the nonvalence bound states of the anions, *Chem. Phys. Rev.* **5**, 041301 (2024).
- [18] C. Anst  ter, G. Mensa-Bonsu, P. Nag, M. Rankovic, T. Kumar, A. Boichenko, A. Bochenkova, J. Fedor, and J. Verlet, Mode-specific vibrational autodetachment following excitation of electronic resonances by electrons and photons, *Phys. Rev. Lett.* **124** (2020).
- [19] M. Rankovic, P. Nag, C. Anst  ter, G. Mensa-Bonsu, T. Kumar, J. Verlet, and J. Fedor, Resonances in nitrobenzene

- probed by the electron attachment to neutral and by the photodetachment from anion, *J. Chem. Phys.* **157** (2022).
- [20] A. Léger, P. Boissel, and L. d'Hendecourt, Predicted fluorescence mechanism in highly isolated molecules: The Poincaré fluorescence, *Phys. Rev. Lett.* **60**, 921 (1988).
- [21] M. Saito, H. Kubota, K. Yamasa, K. Suzuki, T. Majima, and H. Tsuchida, Direct measurement of recurrent fluorescence emission from naphthalene ions, *Phys. Rev. A* **102**, 012820 (2020).
- [22] Y. Liu, C. Li, Z. Ren, S. Yan, and M. R. Bryce, All-organic thermally activated delayed fluorescence materials for organic light-emitting diodes, *Nat. Rev. Mater.* **3**, 18020 (2018).
- [23] J. N. Bull and J. R. R. Verlet, Observation and ultrafast dynamics of a nonvalence correlation-bound state of an anion, *Sci. Adv.* **3**, e1603106 (2017).
- [24] D. H. Kang, J. Kim, and S. K. Kim, Dynamic role of the correlation effect revealed in the exceptionally slow autodetachment rates of the vibrational Feshbach resonances in the dipole-bound state, *Chem. Sci.* **13**, 2714 (2022).
- [25] Jack. Simons and K. D. Jordan, *Ab initio* electronic structure of anions, *Chem. Rev.* **87**, 535 (1987).
- [26] K. D. Jordan and F. Wang, Theory of Dipole-Bound Anions, *Annu. Rev. Phys. Chem.* **54**, 367 (2003).
- [27] C. J. Clarke, E. M. Burrow, and J. R. R. Verlet, The valence electron affinity of uracil determined by anion cluster photoelectron spectroscopy, *Phys. Chem. Chem. Phys.* **26**, 20037 (2024).
- [28] I. Anusiewicz, P. Skurski, and J. Simons, Fate of dipole-bound anion states when hydrated, *J. Phys. Chem. A* **124**, 2064 (2020).
- [29] M. E. Castellani, C. S. Anstöter, and J. R. R. Verlet, On the stability of a dipole-bound state in the presence of a molecule, *Phys. Chem. Chem. Phys.* **21**, 24286 (2019).
- [30] C. J. Clarke, E. M. Burrow, and J. R. R. Verlet, The role of water molecules in the dissociation of an electron-molecule contact pair, *Nat. Commun.* **16**, 2113 (2025).
- [31] M. Allan, Study of triplet states and short-lived negative ions by means of electron impact spectroscopy, *J. Electron Spectrosc. Relat. Phenom.* **48**, 219 (1989).
- [32] K. Regeta and M. Allan, Autodetachment dynamics of acrylonitrile anion revealed by two-dimensional electron impact spectra, *Phys. Rev. Lett.* **110**, 203201 (2013).
- [33] J. Dvořák, M. Ranković, K. Houfek, P. Nag, R. Čurík, J. Fedor, and M. Čížek, Vibronic coupling through the continuum in the $e + \text{CO}_2$ system, *Phys. Rev. Lett.* **129**, 013401 (2022).
- [34] F. Currell and J. Comer, Observation of friction in the nuclear dynamics of CO_2^- near the equilibrium geometry of the negative ion, *Phys. Rev. Lett.* **74**, 1319 (1995).
- [35] T. Reddish, F. Currell, and J. Comer, Studies of the 2 eV shape resonance in N_2 using a two-dimensional scanning technique, *J. Phys. E* **21**, 203 (1988).
- [36] C. S. Anstöter, J. N. Bull, and J. R. R. Verlet, Ultrafast dynamics of temporary anions probed through the prism of photodetachment, *Int. Rev. Phys. Chem.* **35**, 509 (2016).
- [37] C. W. West, J. N. Bull, E. Antonkov, and J. R. R. Verlet, Anion resonances of para-benzoquinone probed by frequency-resolved photoelectron imaging, *J. Phys. Chem. A* **118**, 11346 (2014).
- [38] C. S. Anstöter and J. R. R. Verlet, A Hückel model for the excited-state dynamics of a protein chromophore developed using photoelectron imaging, *Acc. Chem. Res.* **55**, 1205 (2022).
- [39] C. A. Hart, A. W. Schlimgen, D. B. Dao, K. Head-Marsden, and R. Mabbs, The overlooked role of excited anion states in NiO_2 -photodetachment, *J. Chem. Phys.* **160**, 044304 (2024).
- [40] A. S. Case, E. M. Miller, J. P. Martin, Y.-J. Lu, L. Sheps, A. B. McCoy, and W. C. Lineberger, Dynamic Mapping of CN Rotation Following Photoexcitation of ICN-, *Angew. Chem. Int. Ed.* **51**, 2651 (2012).
- [41] J. Kočíšek, A. Pysanenko, M. Fárník, and J. Fedor, Microhydration prevents fragmentation of uracil and thymine by low-energy electrons, *J. Phys. Chem. Lett.* **7**, 3401 (2016).
- [42] J. Poštulka, P. Slavíček, J. Fedor, M. Fárník, and J. Kočíšek, Energy transfer in microhydrated uracil, 5-fluorouracil, and 5-bromouracil, *J. Phys. Chem. B* **121**, 8965 (2017).
- [43] A. Lietard, G. Mensa-Bonsu, and J. R. R. Verlet, The effect of solvation on electron capture revealed using anion two-dimensional photoelectron spectroscopy, *Nat. Chem.* **13**, 737 (2021).
- [44] A. Lietard and J. R. R. Verlet, Effect of microhydration on the temporary anion states of pyrene, *J. Phys. Chem. Lett.* **13**, 3529 (2022).
- [45] G. A. Cooper, C. J. Clarke, and J. R. R. Verlet, Low-energy shape resonances of a nucleobase in water, *J. Am. Chem. Soc.* **145**, 1319 (2023).
- [46] J. P. Rogers, C. S. Anstöter, J. N. Bull, B. F. E. Curchod, and J. R. R. Verlet, Photoelectron spectroscopy of the hexafluorobenzene cluster anions: $(\text{C}_6\text{F}_6)_n^-$ ($n = 1 - 5$) and $\text{I} - (\text{C}_6\text{F}_6)$, *J. Phys. Chem. A* **123**, 1602 (2019).
- [47] U. Even, The Even-Lavie valve as a source for high intensity supersonic beam, *EPJ Tech. Instrum.* **2**, 1 (2015).
- [48] W. C. Wiley and I. H. McLaren, Time-of-flight mass spectrometer with improved resolution, *Rev. Sci. Instrum.* **26**, 1150 (1955).
- [49] A. T. J. B. Eppink and D. H. Parker, Velocity map imaging of ions and electrons using electrostatic lenses: Application in photoelectron and photofragment ion imaging of molecular oxygen, *Rev. Sci. Instrum.* **68**, 3477 (1997).
- [50] G. M. Roberts, J. L. Nixon, J. Lecointre, E. Wrede, and J. R. R. Verlet, Toward real-time charged-particle image reconstruction using polar onion-peeling, *Rev. Sci. Instrum.* **80**, 053104 (2009).
- [51] V. G. Osipov, V. A. Shlyapochnikov, and E. F. Ponizovtsev, Vibrational spectra of aromatic nitro compounds, *J. Appl. Spectrosc.* **8**, 598 (1968).
- [52] J. H. S. Green and D. J. Harrison, Vibrational spectra of benzene derivatives—X: Monosubstituted nitrobenzenes, *Spectrochim. Acta Part Mol. Spectrosc.* **26**, 1925 (1970).
- [53] M. J. Frisch *et al.*, Gaussian 16 Rev. C.01 Wallingford, CT 2016 (2016).
- [54] T. H. Dunning Jr., Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, *J. Chem. Phys.* **90**, 1007 (1989).
- [55] F. Weigend, A. Köhn, and C. Hättig, Efficient use of the correlation consistent basis sets in resolution of the identity MP2 calculations, *J. Chem. Phys.* **116**, 3175 (2002).

- [56] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/zfxx-8r4x> for additional photoelectron spectra, RICVAD fits, and the results of *ab initio* calculations.
- [57] A. Modellia and M. Venuti, Empty level structure and dissociative electron attachment in gas-phase nitro derivatives, *Int. J. Mass Spectrom.* **205**, 7 (2001).
- [58] N. L. Asfandiarov, S. A. Pshenichnyuk, V. G. Lukin, I. A. Pshenichnyuk, A. Modelli, and Š. Matejčík, Temporary anion states and dissociative electron attachment to nitrobenzene derivatives, *Int. J. Mass Spectrom.* **264**, 22 (2007).
- [59] J. Schiedt, R. Weinkauff, D. M. Neumark, and E. W. Schlag, Anion spectroscopy of uracil, thymine and the amino-oxo and amino-hydroxy tautomers of cytosine and their water clusters, *Chem. Phys.* **239**, 511 (1998).
- [60] V. Periquet, A. Moreau, S. Carles, J. P. Schermann, and C. Desfrancois, Cluster size effects upon anion solvation of N-heterocyclic molecules and nucleic acid bases, *J. Electron Spectrosc. Relat. Phenom.* **106**, 141 (2000).
- [61] S. Eustis, D. Wang, S. Lyapustina, and K. H. Bowen, Photoelectron spectroscopy of hydrated adenine anions, *J. Chem. Phys.* **127**, 224309 (2007).
- [62] J. Q. Chambers and R. N. Adams, Solvent effects on the visible spectra of nitrobenzene anion radicals, *Mol. Phys.* **9**, 413 (1965).
- [63] J. Simons, Propensity rules for vibration-induced electron detachment of anions, *J. Am. Chem. Soc.* **103**, 3971 (1981).
- [64] D. H. Kang and S. K. Kim, Reaction dynamics of the nonvalence bound states of the anions, *Chem. Phys. Rev.* **5**, 041301 (2024).
- [65] R. S. Berry, Ionization of molecules at low energies, *J. Chem. Phys.* **45**, 1228 (1966).
- [66] C. S. Anstöter and J. R. R. Verlet, Gas-phase synthesis and characterization of the Methyl-2,2-dicyanoacetate anion using photoelectron imaging and dipole-bound state autodetachment, *J. Phys. Chem. Lett.* **11**, 6456 (2020).
- [67] H.-T. Liu, C.-G. Ning, D.-L. Huang, P. D. Dau, and L.-S. Wang, Observation of mode-specific vibrational autodetachment from dipole-bound states of cold anions, *Angew. Chem. Int. Ed.* **52**, 8976 (2013).
- [68] C. Desfrancois, V. Périquet, S. A. Lyapustina, T. P. Lippa, D. W. Robinson, K. H. Bowen, H. Nonaka, and R. N. Compton, Electron binding to valence and multipole states of molecules: Nitrobenzene, para- and meta-dinitrobenzenes, *J. Chem. Phys.* **111**, 4569 (1999).
- [69] C. Anstöter, T. Gartmann, L. Stanley, A. Bochenkova, and J. Verlet, Electronic structure of the *para*-dinitrobenzene radical anion: A combined 2D photoelectron imaging and computational study, *Phys. Chem. Chem. Phys.* **20**, 24019 (2018).
- [70] D. A. Horke, Q. Li, L. Blancafort, and J. R. R. Verlet, Ultrafast above-threshold dynamics of the radical anion of a prototypical quinone electron-acceptor, *Nat. Chem.* **5**, 711 (2013).
- [71] C. R. Sagan, C. S. Anstöter, M. Thodika, K. D. Wilson, S. Matsika, and E. Garand, Spectroscopy and theoretical modeling of tetracene anion resonances, *J. Phys. Chem. Lett.* **13**, 10245 (2022).
- [72] D. Loru, A. L. Steber, C. Pérez, D. A. Obenchain, B. Temelso, J. C. López, and M. Schnell, Quantum tunneling facilitates water motion across the surface of phenanthrene, *J. Am. Chem. Soc.* **145**, 17201 (2023).
- [73] C. Pérez, A. L. Steber, A. M. Rijs, B. Temelso, G. C. Shields, J. C. Lopez, Z. Kisiel, and M. Schnell, Corannulene and its complex with water: A tiny cup of water, *Phys. Chem. Chem. Phys.* **19**, 14214 (2017).
- [74] E. M. Burrow, C. J. Clarke, and J. R. R. Verlet, Data for effect of incremental hydration on reverse internal conversion vibrational autodetachment of an anion, [10.5281/zenodo.16743696](https://zenodo.org/record/16743696).