

# High-Resolution Photoelectron Spectroscopy of Vibrationally Excited Vinoxide Anions

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## Abstract

High-resolution photoelectron spectra of vibrationally pre-excited vinoxide anions ( $\text{CH}_2\text{CHO}^-$ ) are reported using the recently developed IR-cryo-SEVI technique. This method is combined with a newly developed implementation of vibrational perturbation theory that can readily identify relevant anharmonic couplings among nearly degenerate vibrational states. IR-cryo-SEVI spectra are obtained by resonant infrared excitation of vinoxide anions via the fundamental C-O ( $\nu_4$ ,  $1570\text{ cm}^{-1}$ ) or isolated C-H ( $\nu_3$ ,  $2546\text{ cm}^{-1}$ ) stretching vibrations prior to photodetachment. Excitation of the  $\nu_4$  mode leads to a well-resolved photoelectron spectrum that is in excellent agreement with a harmonic Franck-Condon simulation. Excitation of the higher energy  $\nu_3$  mode results in a more complicated spectrum that requires consideration of the calculated anharmonic resonances in both the anion and neutral. From this analysis, information about the zeroth-order states that contribute to the nominal  $\nu_3$  wavefunction in the anion is obtained. In the neutral, we observe anharmonic splitting of the  $\nu_3$  fundamental into a polyad feature with peaks at  $2737(22)$ ,  $2835(18)$  and  $2910(12)\text{ cm}^{-1}$ , for which only the center frequency has been previously reported. Overall, nine out of the twelve fundamental frequencies of the vinoxyl radical are extracted from the IR-cryo-SEVI and ground state cryo-SEVI spectra, most of which are consistent with previous measurements. However, we provide a new estimate of the  $\nu_5$  ( $\text{CH}_2$  scissoring) fundamental frequency at  $1395(11)\text{ cm}^{-1}$  and attribute the large difference with previously reported values to a Fermi resonance with the  $2\nu_{11}$  overtone ( $\text{CH}_2$  wagging).

## 1. Introduction

Anion photoelectron spectroscopy (PES) is a versatile technique that has been used to probe spectroscopy and energetics of reactive free radicals,<sup>1,2</sup> a wide range of clusters,<sup>3-6</sup> and transition states for unimolecular and bimolecular reactions.<sup>7-9</sup> It enables precise measurements of electron affinities for atomic and molecular species,<sup>10</sup> and is capable of probing electronic and vibrational structure in the ground and excited electronic states of neutral species that are accessible via photodetachment. The selection rules for PES are more relaxed compared to conventional bound-bound electronic absorption spectroscopy due to the angular momentum transferred to the photoelectron. Moreover, photodetachment does not require resonant excitation as a mismatch between the photon and transition energy can be compensated by the kinetic energy of the outgoing electron.<sup>9, 11, 12</sup> Our laboratory has devoted considerable effort to improving the energy resolution of anion PES through the technique of cryo-SEVI (slow photoelectron velocity-map imaging of cryogenically cooled anions), which yields vibrationally resolved spectra with a resolution down to  $\sim 1 \text{ cm}^{-1}$ .<sup>13-15</sup> At this higher resolution, one can resolve progressions in multiple vibrational modes that could not be seen in more conventional PES experiments.<sup>16, 17</sup> Here, we present a significant extension of cryo-SEVI by exploring the effects of vibrational pre-excitation of a polyatomic anion, the vinoxide anion ( $\text{CH}_2\text{CHO}^-$ ), prior to photodetachment.

The motivation for vibrational pre-excitation is evident from Figure 1. In anion PES, the intensities of transitions from the anion ground state to vibrationally excited neutral levels are typically governed by Franck-Condon (FC) factors, in which case one only observes progressions in those totally symmetric vibrational modes for which there is a normal coordinate displacement upon photodetachment. There is no such displacement for symmetry reasons in non-totally symmetric modes, while for totally symmetric modes comprising C-H, O-H, and N-H stretches, the changes in bond lengths are generally very small.<sup>18-20</sup> Hence, the situation on the left side of Figure 1 holds; the transition strength from the anion ground state to the  $\nu = 1$  level of a non-totally symmetric mode or a mode in which there is no normal coordinate displacement is either zero by symmetry or negligibly small. However, excitation of the  $\nu = 1$  level of one of these modes in the anion results in a fully FC-allowed transition to the neutral  $\nu = 1$  level, as shown on the right side of Figure 1, leading to new features in the photoelectron spectrum.

We recently reported cryo-SEVI spectra of  $\text{OH}^-$ , in which  $\text{OH}^-$  was rovibrationally excited from the  $(v = 0, J = 0)$  ground state to the  $(v = 1, J = 1)$  level before photodetachment by an additional infrared (IR) laser.<sup>21</sup> This experiment was the first demonstration of cryo-SEVI in combination with prior infrared excitation (IR-cryo-SEVI), but the application of this approach to studies of polyatomic molecules has not yet been reported. There are several fundamental challenges to such an experiment. First, vibrational frequencies in polyatomic anions are generally less well-characterized compared to their neutral counterparts. Secondly, the rotational level structure of a polyatomic molecule is denser compared to  $\text{OH}^-$ . As a result, one does not expect to be able to resolve individual rotational transitions, due to the  $\sim 1 \text{ cm}^{-1}$  resolution in conventional cryo-SEVI as well as the  $\sim 3 \text{ cm}^{-1}$  excitation laser bandwidth used in the IR-cryo-SEVI experiment. Finally, anharmonic coupling in the anion can result in a vibrationally excited state that shows contributions from several zeroth-order states, each of which has a distinct contribution to the photoelectron spectrum. This may lead to a more complex spectrum than implied by Figure 1. The effects of anharmonic coupling in the electronic ground states of molecules have been investigated by a variety of frequency-resolved techniques, including high-resolution IR absorption spectroscopy, overtone pumping, dispersed IR fluorescence, stimulated emission pumping and other double-resonance techniques.<sup>22-24</sup> Depending on the extent of anharmonic coupling, IR-cryo-SEVI could thus provide a new approach to simultaneously obtain state-specific information on anharmonic coupling in the ground electronic states of both the anion and neutral.

In the presence of anharmonic coupling, assignment of IR-cryo-SEVI spectra requires extensions to existing theoretical methods, as one observes a transition from a vibrationally excited state in the anion to a vibrationally excited state in the neutral. Therefore, the theoretical treatment requires the evaluation of wavefunctions and energies for the vibrational states of both the anion and neutral, as well as transition intensities between these states. In the simplest approach, one would model the vibrations as harmonic oscillators. Existing software packages<sup>25,26</sup> can then be used to evaluate the FC overlap between the harmonic wavefunctions in the anion and neutral. Including the effects of state-mixing among the vibrational states, however, requires methods beyond the harmonic approximation, done here within the framework of nearly-degenerate vibrational perturbation theory (VPT).<sup>27-29</sup>

The vinoxide anion ( $\text{CH}_2\text{CHO}^-$ ) is an appropriate system to explore with IR-cryo-SEVI owing to its well-studied photodetachment spectrum measured in several laboratories,<sup>30-36</sup> including a high-

resolution SEVI study from our group.<sup>36</sup> The neutral vinyoxy radical is relevant to combustion chemistry, appearing as an intermediate in the oxidation of terminal alkenes,<sup>37</sup> and its dissociation dynamics have been studied in detail.<sup>38-41</sup> The geometry of the vinyoxy radical reflects contributions from two planar resonance structures. The dominant contribution to its  $\tilde{X}^2A''$  ground state comes from a formyl methyl structure ( $\text{CH}_2\text{CH}=\text{O}$ ), with the free electron on the methylene carbon, rather than the vinyoxy structure ( $\text{CH}_2=\text{CHO}$ ) implied by its name where the unpaired electron would be located on the oxygen atom. This structure was recognized early on in matrix IR absorption studies,<sup>42</sup> and is consistent with high-level ab initio calculations<sup>43</sup> and the spin density on the methylene carbon obtained from microwave spectra.<sup>44, 45</sup> The vinyoxy anion in its  $\tilde{X}^1A'$  ground state has a similar geometry to the radical with slightly longer C-O and slightly shorter C-C bond lengths based on calculations, more resembling the vinyoxy structure ( $\text{CH}_2=\text{CHO}$ ).<sup>34, 36, 46</sup>

Several spectroscopic techniques have been applied to study the vibrational structure of the vinyoxy radical, but the determination of fundamental frequencies for its C-H stretching vibrations has been surprisingly challenging. IR absorption studies of vinyoxy radicals isolated in an Ar matrix<sup>42</sup> could not probe any of the C-H stretch fundamental frequencies ( $\nu_1$ - $\nu_3$ ) due to technical limitations. The vibrational structure of the ground state was further investigated in the gas phase by multiple laser-induced fluorescence (LIF) studies based on  $\tilde{B}^2A'' - \tilde{X}^2A''$  transitions.<sup>47-51</sup> Early LIF studies<sup>47, 48</sup> focused mainly on the C-O stretching ( $\nu_4$ ), C-C stretching ( $\nu_7$ ) and C-C-O ( $\nu_9$ ) bending vibrations, which show the highest FC activity owing to the different geometry of the C-C-C backbone in the ground and excited electronic state.<sup>38, 52</sup> Reanalysis of this LIF data<sup>49</sup> and additional LIF measurements<sup>50, 51</sup> enabled assignments of the  $\nu_4 - \nu_{12}$  modes. However, the C-H stretch fundamentals ( $\nu_1 - \nu_3$ ) are not FC-active in those LIF experiments and have not been observed. To date only a single measurement of the  $\nu_3$  fundamental based on multi-pass IR laser absorption spectroscopy in a supersonic jet has been reported, placing the band origin at  $2827.913 \text{ cm}^{-1}$ .<sup>53</sup>

The vinyoxy anion has also been the focus of several spectroscopic investigations. Early reports of its photodetachment spectra into the neutral ground state yielded an estimate of the electron affinity but showed little vibrational structure.<sup>30, 32</sup> In addition, a dipole-bound anion state exists only a few  $\text{cm}^{-1}$  below the detachment threshold.<sup>31, 33</sup> Photodetachment spectra encompassing the  $\tilde{X}^2A''$  and  $\tilde{A}^2A'$  states of the neutral were reported by Continetti and co-workers, showing some vibrationally resolved features.<sup>34, 35</sup> SEVI spectra have been reported for vinyoxy<sup>36</sup> and two of its

derivatives<sup>54, 55</sup>. The SEVI spectra by Yacovitch *et al.*<sup>36</sup> resolved vibrational levels within the  $\tilde{X}^2A''$  and  $\tilde{A}^2A'$  states of the vinoxy radical and provided a precise determination of its electron affinity (14719(9) cm<sup>-1</sup>). The ground state spectrum showed extended activity in the neutral  $\nu_4$ ,  $\nu_7$  and  $\nu_9$  modes. This work was done prior to incorporation of cryogenic cooling into the instrument, and hot band transitions due to incomplete cooling complicated the assignment for low intensity lines.

In this work, we report cryo-SEVI spectra of vinoxide selectively prepared in its vibrational ground state as well as in vibrationally excited states by IR laser excitation of the  $\nu_4$  (C-O stretching) and  $\nu_3$  (C-H stretching) fundamentals at 1570 and 2546 cm<sup>-1</sup>, respectively, prior to photodetachment. We show that the  $\nu_4$  vibration in the anion is weakly coupled to other vibrations whereas excitation of the  $\nu_3$  fundamental followed by photodetachment shows evidence for strong anharmonic coupling within the anion and the neutral, leading to complex spectra that require analysis beyond harmonic FC simulations. Assignment of all spectra presented here allows us to extract fundamental vibrational frequencies of the vinoxy radical for all vibrational modes except for the two higher frequency C-H stretching vibrations ( $\nu_1$ ,  $\nu_2$ ) and the isolated C-H wagging vibration ( $\nu_{10}$ ). We discuss deviations between our observations and previous observations for the  $\nu_3$  and  $\nu_5$  fundamentals as well as state-specific information on anharmonic coupling in both the anion and neutral extracted from the  $\nu_3$  IR-cryo-SEVI spectra. Finally, we consider the potential of using IR-cryo-SEVI in combination with our implementation of VPT to investigate other polyatomic systems.

## 2. Experimental Methods

The apparatus for high-resolution photoelectron spectroscopy based on anion cryo-SEVI has been described in detail elsewhere.<sup>13-15, 21</sup> To make vinoxide anions, helium gas mixed with trace amounts of acetaldehyde and N<sub>2</sub>O is expanded through a pulsed Even-Lavie valve coupled to a filament ionizer.<sup>56</sup> Dissociative electron attachment to N<sub>2</sub>O produces O<sup>-</sup> ions that abstract a methyl proton from acetaldehyde to form C<sub>2</sub>H<sub>3</sub>O<sup>-</sup>. The anions pass through a skimmer into a guiding radiofrequency (RF) hexapole and then an RF quadrupole filter for initial mass selection. The mass-selected ions enter a linear octupole ion trap held at 5 K, in which they are stored for ~40 ms while being cooled through collisions with a H<sub>2</sub>/He buffer gas mixture (20%/80%).<sup>14</sup> The cooled anions are extracted into an orthogonal Wiley-McLaren time-of-flight mass spectrometer.<sup>57</sup> At the end of

a  $\sim 2$  m long flight path, ions of the desired mass are photodetached by an appropriately timed laser pulse within a 7-plate velocity-map imaging (VMI) lens assembly designed to optimize resolution for slow electrons.<sup>15</sup> A set of gated deflector plates only allows ions of approximately the correct mass to enter the VMI region. For photodetachment, the output of a dye laser (Radiant Dyes NarrowScan) pumped by the second harmonic of a nanosecond Nd:YAG laser (Spectra-Physics Quanta-Ray PRO-290), operating at 20 Hz, is used. The detached photoelectrons are mapped onto a position-sensitive imaging detector comprising two chevron-stacked microchannel plates and a phosphor screen. Images are acquired at a repetition rate of 20 Hz with a CCD camera (768 $\times$ 768 pixels). Individual electron spots are event-counted and binned onto a 1024 $\times$ 1024 grid using the hybrid gradient-center of mass (HGCM) centroiding algorithm introduced in Ref. 58.

The addition of an OPO/OPA IR laser system (LaserVision), pumped by a Nd:YAG laser (Continuum SureLite SLIII-EX), for IR-cryo-SEVI has been previously described.<sup>21</sup> A schematic of the optical setup, including some additional details, can be found in Figure S1. The OPO/OPA is operated at half the repetition rate of the detachment laser (10 Hz) to enable a direct, shot-to-shot comparison between photodetachment with (“IR on”) and without IR pre-excitation (“IR off”). IR wavelengths are calculated from the near-IR frequency of the signal in the OPO stage determined with a wavemeter (Coherent WaveMaster). To excite the  $\nu_3$  vibration of vinoxide at  $2546\pm 1$   $\text{cm}^{-1}$ , we directly use the idler output of the OPA at a typical pulse energy of  $\sim 2.0$  mJ. To excite the  $\nu_4$  vibration at  $1570\pm 2$   $\text{cm}^{-1}$ , we add an additional difference frequency generation (DFG) stage to mix the OPA signal and idler in an AgGaSe<sub>2</sub> crystal, resulting in mid-IR radiation with a typical pulse energy of 1.0-1.6 mJ. For the detachment laser, pulse energies of 2-4.5 mJ were used.

The counterpropagating IR and detachment laser beams are focused and overlapped in the VMI region of the vacuum chamber using CaF<sub>2</sub> lenses with focal lengths of 500 and 1000 mm, respectively. The IR laser focus diameter is estimated as 0.5 and 0.9 mm at 2550 and 1550  $\text{cm}^{-1}$ , respectively, ensuring that the IR excitation region is larger than that of the detachment laser for which the estimated focus diameter is below 0.2 mm. Both laser pulses are also temporally overlapped on a photodiode outside the vacuum chamber using the visible dye laser light and near-IR light from the OPO/OPA.

Photoelectron velocity-map images are processed using the Maximum Entropy Velocity Legendre Reconstruction (MEVELER) algorithm<sup>59</sup> to obtain reconstructed radial and angular distributions.

The radial distribution of the spectrum is related to the electron kinetic energy (eKE) through a calibration based on the well-known photodetachment transitions for atomic  $O^-$  at various photon energies.<sup>60</sup> The electron binding energy (eBE) is obtained from the eKE and the photon energy,  $h\nu$ , by  $eBE = h\nu - eKE$ . High-resolution scans are composed of individual scans at different photon energies, close to the transitions of interest, to benefit from the improved resolutions of our setup for slow photoelectrons. The intensities of these scans are scaled to match a lower resolution overview spectrum obtained at a photon energy that is sufficiently high to access most (if not all) of the electronic band of interest. To account for the relatively low signals that appear for new features after IR pre-excitation, 4-5 images were typically acquired for the same photon energy under comparable conditions and individually reconstructed. The resulting photoelectron spectra were then added.

From the reconstructed angular distribution, anisotropy parameters,  $\beta$ , can be obtained, which contribute to the differential detachment cross section according to eq 1 for linearly polarized light.<sup>61, 62</sup>

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{\text{total}}}{4\pi} (1 + \beta P_2(\cos \theta)). \quad (1)$$

Here,  $\sigma_{\text{total}}$  is the total photodetachment cross section,  $P_2(x)$  is a second-order Legendre polynomial and  $\theta$  describes the angle between the direction of the detached electron and the polarization vector of the laser light. The anisotropy parameter lies between  $-1$  and  $+2$  for perpendicular and parallel detachment, respectively. Its dependence on eKE gives information on the electronic state and molecular orbital from which photodetachment occurs.

### 3. Computational Details

#### 3.1. Generalized Vibrational Perturbation Theory Calculations

As will be seen below, excitation of the  $\nu_3$  mode of the anion leads to photoelectron spectra that cannot be described by simple harmonic analysis. Analysis of these spectra requires a way to account for anharmonic coupling in both the anion and neutral. To aid in the interpretation of these effects, vibrational perturbation theory (VPT)<sup>28, 29, 63</sup> calculations were performed using `PyVPTn`,<sup>64, 65</sup> which provides an implementation of VPT in a matrix representation. All VPT calculations were performed using normal mode coordinates that are constructed from linear combinations of valence coordinates. The valence coordinates used to construct the normal modes and their values at the

minimum energy structures are provided in Table S1. The normal modes of the anion and neutral are illustrated in Figures S2 and S3. The requisite quartic expansion of the potential in these coordinates was obtained at the B2PLYP-D3/aug-cc-pVTZ level of theory and basis by numerically evaluating the first and second derivatives of the Hessian with respect to each of the  $3N-6$  normal modes, as implemented in Gaussian 16.<sup>66</sup> The choice to use this level of theory is based on its effectiveness for studies of similar organic radicals.<sup>67</sup>

Critical to these calculations is the ability to identify nearly degenerate states.<sup>27, 29, 68-70</sup> In vibrational perturbation theory without the consideration of resonances, corrections to the zeroth-order states and energies are obtained as vectors of expansion coefficients in the basis comprised of the zeroth-order states. When resonances are present, this procedure must be modified. For the calculations performed in this study, a resonance between states  $n$  and  $m$  was identified if the expansion coefficient from state  $m$  for the corrections to state  $n$  at any order of correction was greater than 0.3 or *vice versa*. We also introduce the requirement that for a given state of interest, the set of states resonant with this state spans an energy range of no more than  $500\text{ cm}^{-1}$ . These criteria were found to be effective in a previous study.<sup>69</sup> This results in a resonant space consisting of three states for the  $\nu_3$  state in  $\text{H}_2\text{CCHO}^-$  and 31 states that make up the resonant space for the corresponding state in  $\text{H}_2\text{CCHO}$ . Additionally, a resonance between the  $\nu_3$  state and the  $\nu_4 + \nu_8$  state was introduced to the set of nearly degenerate states in the anion resulting in a final resonant space consisting of four states. This resonance is not identified through the resonance criterion introduced earlier, which is based on the ratio of the coupling matrix element involving this pair of states to the difference between their harmonic frequencies; their harmonic frequencies differ by  $\sim 140\text{ cm}^{-1}$  while the matrix element is only  $\sim 7\text{ cm}^{-1}$ . However, the difference between the anharmonic frequencies of these two states reduces the energy difference to only  $\sim 10\text{ cm}^{-1}$ , leading to a strong resonance interaction between these two states once diagonal anharmonicities are considered.

Once the resonances are identified, a second VPT calculation is performed in which all nearly degenerate states are projected out of the basis. This calculation provides the deperturbed energies of these nearly degenerate states as well as the matrix elements of the Hamiltonian in the basis of these deperturbed states. The Hamiltonian, expressed in the basis of deperturbed states, is then diagonalized to obtain the anharmonically coupled vibrational wavefunctions and corresponding frequencies. This corresponds to a  $4\times 4$  matrix for the  $\nu_3$  state in  $\text{H}_2\text{CCHO}^-$  and a  $31\times 31$  matrix for



H<sub>2</sub>CCHO. Additional details of this approach for identifying resonances and the evaluation of the Hamiltonian matrix are described elsewhere.<sup>69</sup> The calculated coupling matrices and corresponding coefficients used to express the vibrational wavefunctions in the basis of deperturbed states can be found in the SI in a separate excel spreadsheet.

Finally, some of the diagonal elements of these coupling matrices in the basis of nearly degenerate states are shifted, as detailed in Section S1.1 (supported by Figures S4 and S5). For the neutral, this includes a shift of  $-50\text{ cm}^{-1}$  for the harmonic  $\nu_4$  frequency to match the calculated  $\nu_4$  fundamental frequency with the experimental value, affecting the deperturbed frequencies of all modes that involve  $\nu_4$  excitation in a similar manner. For the anion, the deperturbed frequencies of the  $\nu_4 + \nu_8$  and  $2\nu_6$  states were directly shifted by about  $-20$  and  $+40\text{ cm}^{-1}$ , respectively, motivated by observations in the photodetachment spectrum following  $\nu_3$  excitation. This is necessary as the extent of the couplings between the states can be sensitive to small shifts in their energies and induce variations from the experimentally observed frequencies and spectra. A similar strategy was employed in a recent study of the vibrational spectrum of complexes formed between halide ions and HOCl.<sup>71</sup>

### 3.2. Calculation of Anharmonic Franck-Condon Spectra

Franck-Condon (FC) spectra, including Duschinsky rotations between all modes,<sup>72</sup> were simulated using ezFCF 1.2 within the harmonic approximation.<sup>25,73</sup> Those spectra were calculated for the vibrational ground state and selected vibrationally excited states of the anion. FC spectra of vibrationally excited anion states with up to three quanta were obtained by simulating a full spectrum at 300 K and extracting the FC factors for the transitions of interest. Unless otherwise stated, eBEs were calculated based on the anharmonic anion and neutral frequencies from the B2PLYP-D3/aug-cc-pVTZ calculations. Note, however, that the corresponding calculated spectra still rely on FC factors calculated with harmonic wavefunctions. All FC calculations were performed using Cartesian coordinates for the minimum energy structures (Table S2) and normal coordinates.

For simulation of the  $\nu_3$  IR-cryo-SEVI spectra, a different approach is used to account for anharmonic corrections to peak positions (see Section S1.2) and anharmonic intensities (described in the following). There, anion and neutral wavefunctions are considered, which each contain

contributions from various anharmonically coupled zeroth-order states. For the anion, the vibrationally excited state is described by

$$|\chi_i''\rangle = \sum_j c_j'' |\phi_j''\rangle, \quad (2)$$

where the  $|\phi_j''\rangle$  comprise the set of states that are nearly degenerate with the state of interest, here the  $\nu_3$  mode in the anion. This set of states is identified in the VPT2 calculation (see Section 3.1), and the elements of the Hamiltonian matrix, expressed in this basis, are obtained from the deperturbed VPT2 calculation. The mixing coefficients  $c_j''$  are obtained from diagonalization of this Hamiltonian matrix. Equivalently, we define the anharmonic vibrational wavefunction in the neutral as

$$|\chi_f'\rangle = \sum_k c_k' |\phi_k'\rangle. \quad (3)$$

Here,  $c_k'$  and  $|\phi_k'\rangle$  provide the mixing coefficients and zeroth-order states within the resonant space of the final vibrational state in the neutral. The anharmonic FC factors, which are the square of the  $\langle\chi_f'|\chi_i''\rangle$  matrix elements, are thus given by eq 4. The summation runs over all zeroth-order states in the resonant space of the anion (index  $j$ ) and the neutral (index  $k$ ).

$$|\langle\chi_f'|\chi_i''\rangle|^2 = \left| \sum_{j,k} c_k' c_j'' \langle\phi_k'|\phi_j''\rangle \right|^2. \quad (4)$$

For the evaluation of these FC factors, we approximate the actual zeroth-order state wavefunctions  $|\phi_j''\rangle$  and  $|\phi_k'\rangle$ , obtained from the deperturbed VPT2 calculations, by the corresponding harmonic wavefunctions  $|\phi_{h,j}''\rangle$  and  $|\phi_{h,k}'\rangle$ , which will be referred to as zeroth-order states in the following:

$$I_{i,f} = \left| \sum_{j,k} c_k' c_j'' \langle\phi_{h,k}'|\phi_{h,j}''\rangle \right|^2. \quad (5)$$

The quantity  $I_{i,f}$  provides an approximate way to evaluate anharmonic FC factors that include state mixing based on harmonic zeroth-order states and it is used for the anharmonic FC simulations shown in the present work. The harmonic FC overlaps,  $\langle\phi_{h,k}'|\phi_{h,j}''\rangle$ , are again calculated with ezFCF. Note that eq 5 is expected to provide a good approximation to eq 4 because  $|\phi_j''\rangle$  and  $|\phi_k'\rangle$  result from deperturbed VPT calculations, making the contributions from other states to these

wavefunctions small compared to the leading term in the expansion. This approach to calculating anharmonic FCFs (including Duschinsky rotations) is similar to the ones described in Refs. 74 and 75 but relies on anharmonic wavefunctions obtained from vibrational perturbation theory instead of variational anharmonic calculations.

For the special case that the neutral wavefunction can be represented by a single zeroth-order state,  $|\chi'_f\rangle \approx |\phi'_{h,f}\rangle$ , eq 5 reduces to:

$$I_{i,f}^{(\text{uc})} = \left| \sum_j c_j'' \langle \phi'_{h,f} | \phi''_{h,j} \rangle \right|^2. \quad (6)$$

## 4. Results

### 4.1. Photoelectron spectra of ground state and vibrationally excited vinoxide

#### Photoelectron spectra of ground state vinoxide

The cryo-SEVI spectrum of vinoxide in its vibrational ground state is presented in Figure 2, showing an overview spectrum (blue trace) and high-resolution scans (black traces). Peak positions obtained from Gaussian fits to the high-resolution spectra are listed in Table 1. Note that these spectra are collected at the same time as the data for the vibrationally excited ions.

The cryo-SEVI spectrum is dominated by a few intense features, labeled “An”, that agree well with the main features observed in previous SEVI measurements when using the overview spectrum in Figure 2 for comparison.<sup>36</sup> Some features in the spectrum consist of two peaks, showing either a shoulder at low eBE (A4/5 and A8/9) or a resolved doublet in the high-resolution spectra (A6/7), not previously resolved in Ref. 36. A1 is readily assigned to the vibrational origin. As also reported in Ref. 36, the intense peaks A2, A3 and A6 clearly form a progression in the  $\nu_9$  mode with spacing  $\sim 500 \text{ cm}^{-1}$ . Other assignments can be found in Table 1 and will be discussed in more detail in Section 4.2. In addition, the main features all share the same anisotropy parameter  $\beta$  as a function of eKE (see Figure S6). An additional set of much less intense features is observed and labeled “an”. For those weak features, another progression (a1, a3, a5) with spacing  $\sim 400 \text{ cm}^{-1}$  is identified.

### **Pre-excitation of the CO stretching mode ( $\nu_4$ IR-cryo-SEVI spectrum)**

Figure 3(a) shows an “IR off” velocity-map image while Figure 3(b) shows the corresponding “IR on” image with the IR laser tuned to the C-O stretching ( $\nu_4$ ) fundamental at  $1570\text{ cm}^{-1}$ . Note that the “IR on” and “IR off” images, presented with a logarithmic intensity scale, are acquired simultaneously under identical experimental conditions, which allows for a direct comparison (see Section 2). Clearly, additional ring features at larger radii appear upon vibrational excitation. The corresponding transitions are more easily seen by comparing the high-resolution cryo-SEVI spectra under “IR on” and “IR off” conditions in Figure 3(c), which are obtained from reconstruction of the corresponding velocity-map images. Five additional peaks appear at eBEs below the vibrational origin (A1) upon vibrational excitation. In tandem, new peaks are observed above the vibrational origin and all peaks that are present in the ground state spectrum are depleted upon IR excitation. The integral of the vibrational origin (peak A1), for example, decreases by  $\sim 14.5\%$ .

Figure 3d shows the corresponding difference spectra (“IR on” – “IR off”) to better distinguish additional peaks arising from IR pre-excitation (positive features) and depletion of peaks in the ground state spectrum (negative features). To first approximation, the spectrum of the vibrationally excited molecules (Figure 3d) looks similar to the ground state spectrum (black trace in Figure 3c) but is shifted to lower eBE, where peak B1 at  $13167\text{ cm}^{-1}$  marks the onset of the spectrum. Since peak B1 is shifted by  $-1554\text{ cm}^{-1}$  relative to the vibrational origin, it is assigned by inspection to the  $4_1^0$  transition. Closer inspection of the difference spectra (Figure 3d) reveals a progression (B1, B2, B4) with a spacing of  $\sim 500\text{ cm}^{-1}$ , similar to the one in the ground state spectrum. Peaks B5 and B7 as well as peaks B6, B8 and B9 form similar progressions with roughly the same spacing. The shapes of peaks B6, B8 and B9 are asymmetric due to overlap with nearby, depleted ground state features, which makes a precise determination of their peak frequencies difficult. The full assignment of the features in Figure 3d, shown in Table 2 and based on the FC simulation in Figure 3e, will be discussed in Section 4.2.

### **Pre-excitation of the CH stretching mode ( $\nu_3$ IR-cryo-SEVI spectrum)**

IR-cryo-SEVI spectra of vinoxide molecules excited along the C-H stretching mode ( $\nu_3$ ) are shown in Figure 4a (red trace) together with the simultaneously measured ground state spectra (black trace). The corresponding difference spectrum is shown in Figure 4b. As in Figure 3, significant depletion of the ground state features – showing an integrated depletion of  $\sim 33.5\%$  for the

vibrational origin – is observed and indicates strong population of the excited vibrational level. In contrast to the  $\nu_4$  IR-cryo-SEVI spectrum, the  $\nu_3$  spectrum does not appear to be a shifted ground state spectrum and is more complicated. Above the vibrational origin (A1), four intense new features on average are observed for each depleted ground state peak, forming a quartet with a 2:2:1:1 intensity pattern. In addition, numerous low intensity features appear at eBEs below the vibrational origin, forming a seemingly irregular spectrum.

The presence of these additional features is a consequence of strong anharmonic coupling between the  $\nu_3$  mode and several other near-resonant vibrational states in both the anion and the neutral. This is illustrated by the comparison between the difference spectrum (Figure 4b) and a FC simulation of the  $\nu_3$  zeroth-order state in the anion based on a deperturbed VPT2 calculation (Figure 4c), which does not consider anharmonic resonances. In the absence of anharmonic coupling, a single peak attributed to the  $3_1^1$  transition would be expected between peaks A1 and A2, owing to the slightly larger  $\nu_3$  frequency in the neutral compared to the anion. Instead, the quartet is observed. It is therefore reasonable to assume that at least some of those four peaks originate from a splitting of the  $3_1^1$  transition due to strong anharmonic coupling in the neutral. In addition, the experimental features at low eBE extend to at most  $2000\text{ cm}^{-1}$  below the vibrational origin (A1). This value is much smaller than the frequency of the  $\nu_3$  CH stretching vibration, and the simulation of the spectrum does not predict any transitions with appreciable FC activity that are shifted by the  $\nu_3$  frequency. Therefore, transitions originating from the uncoupled zeroth-order  $\nu_3$  state in the anion alone cannot explain the observed features below the vibrational origin. Those “hot band” transitions must instead be related to the mixed character of the nominal  $\nu_3$  state in the anion in which other zeroth-order states, e.g. overtones or combination bands, contribute through anharmonic couplings. Transitions from these coupled zeroth-order states then result in the features below the vibrational origin (A1).

### **Infrared action spectra of the $\nu_3$ and $\nu_4$ fundamental**

Our calculations at the B2PLYP-D3/aug-cc-pVTZ level of theory including anharmonicity find two strong IR transitions for the vinoxide anion: the CO stretch ( $\nu_4$ ) at  $1560\text{ cm}^{-1}$  and the CH stretch ( $\nu_3$ ) on the carbonyl at  $2512\text{ cm}^{-1}$ .<sup>76</sup> Experimentally, fundamental frequencies for exciting the  $\nu_3$  and  $\nu_4$  modes in the anion have not been previously reported, and they were determined from the IR action spectra in Figure S7, which peak near the frequencies expected from our

anharmonic frequency calculations. Such action spectra can be obtained with IR-cryo-SEVI by measuring the depletion or increase of the intensity of features in the “IR on” spectra relative to the intensity of the vibrational origin (A1) in the “IR off” spectra as a function of IR wavelength.<sup>21</sup> For the  $\nu_3$  vibration (Figure S7a), the spectrum is based on depletion of the vibrational origin and the peak center is near  $\sim 2540\text{ cm}^{-1}$ . For the  $\nu_4$  vibration (Figure S7b), the spectrum is based on the relative increase of peak B1 and the peak center is near  $1567\text{ cm}^{-1}$ . We did not attempt precise determination of the vibrational band centers and instead tuned the IR laser to frequencies that gave maximum depletion or absorption to obtain optimal signal from excited anions, as indicated by the arrows in Figure S7.

## 4.2. Assignment of the cryo-SEVI and IR-cryo-SEVI spectra

### Ground state cryo-SEVI spectrum

We will first analyze the cryo-SEVI spectrum of ground state vinoxide before considering the IR-cryo-SEVI spectra. Electron binding energies and assignments for the ground state cryo-SEVI spectrum (black traces in Figure 2) are shown in Table 1. The comparison of this spectrum to the previously reported SEVI spectrum without cryogenic cooling of the anion leads to some modified assignments.

The position of the vibrational origin (A1) of  $14721(8)\text{ cm}^{-1}$  gives a slightly refined value for the adiabatic electron affinity of  $1.8252(10)\text{ eV}$ . Comparison to the assignment by Yacovitch *et al.*<sup>36</sup> and a FC simulation shown as a red stick spectrum in Figure 2 readily gives the assignment for most of the main features in the cryo-SEVI spectrum. The  $\sim 500\text{ cm}^{-1}$  progression involving peaks A2, A3 and A6 clearly corresponds to a progression in the CCO bending mode ( $9_0^1$ ,  $9_0^2$  and  $9_0^3$ ) and peak A2 gives a value of  $499(8)\text{ cm}^{-1}$  for the  $\nu_9$  fundamental frequency. Peaks A5 and A7 correspond to excitation of the CC stretching mode ( $7_0^1$ ) and the CO stretching mode ( $4_0^1$ ), with fundamental frequencies of  $1143(8)$  and  $1542(9)\text{ cm}^{-1}$ , respectively. Peak A9 corresponds to  $7_0^1 9_0^1$  excitation.

Several bands that were assigned to hot band transitions in Ref. 36, in which anions were not cryogenically cooled, are absent in the cryo-SEVI spectrum. For example, two previously observed transitions at  $14195$  and  $14918\text{ cm}^{-1}$ , originating from thermal excitation of the lowest frequency  $\nu_9$  and  $\nu_{12}$  modes in the anion, are not observed in the present cryo-SEVI study. We can therefore rule out that any of the smaller features labeled by “an” are related to hot band transitions. Note

that the anion  $\nu_{12}$  mode was labeled as  $\nu_{11}$  in Ref. 36, as its normal mode motion is similar to that of the neutral  $\nu_{11}$  mode.

In addition, we can assign the lower intensity features labeled by “an”, which in Ref. 36 were either obscured by hot band transitions, incorrectly assigned as hot bands, or not identified as peaks. The  $\sim 400\text{ cm}^{-1}$  progression in features a1, a3, and a5 matches well with the calculated frequency of the  $\text{CH}_2$  twisting mode ( $\nu_{12}$ ). While the  $12_0^2$  feature (a3) is predicted by the FC simulation,  $12_0^1$  and  $12_0^3$  (a1 and a5) are odd-quanta transitions in a mode of  $A''$  symmetry and thus symmetry-forbidden. We attribute those odd-quanta transitions to Herzberg-Teller coupling<sup>77</sup> between the  $\tilde{X}^2A''$  ground state and the  $\tilde{A}^2A'$  excited state that lies only  $\sim 1\text{ eV}$  higher in energy. The anisotropy parameters,  $\beta$ , for the  $12_0^1$  transition are indeed systematically more positive than those from the FC-allowed peaks (see Figure S6), consistent with the more positive values of  $\beta$  observed in previous VMI photodetachment studies for the  $\tilde{A}$  state vs. the  $\tilde{X}$  state.<sup>35, 36</sup> For the other low intensity peaks, the  $\beta$ -parameter curves are too noisy for a similar comparison. The position of peak a1 yields  $408(10)\text{ cm}^{-1}$  for the  $\nu_{12}$  frequency, consistent with the experimental values of Refs. 46 and 51. Following a similar argument, we assign peak a2, which is shifted by  $717\text{ cm}^{-1}$  relative to A1, to the symmetry-forbidden  $11_0^1$  transition, in good agreement with the anharmonic  $\nu_{11}$  frequency of  $728\text{ cm}^{-1}$  calculated in the present work. This value is also in excellent agreement with the  $\nu_{11}$  hot band transition observed by Thomas *et al.*<sup>46</sup> and confirms their critical re-analysis of the  $\nu_{11}$  frequency extracted from previous LIF and SEVI data. Peak a7, which shows a shift of  $1373\text{ cm}^{-1}$  and also appears with low intensity in the FC simulation, is assigned to the  $6_0^1$  transition.

With the known frequency of the  $\nu_{12}$  mode, we assign features a4 and a6 to the  $9_0^1 12_0^1$  and  $9_0^1 12_0^2$  combination bands, which are shifted from a1 and a3 by  $\sim 500\text{ cm}^{-1}$ , respectively. The presence of Herzberg-Teller coupling for both the  $\nu_{11}$  and  $\nu_{12}$  modes might also explain the shoulders A4 and A8, which fit well to the expected frequencies of the  $11_0^1 12_0^1$  and  $9_0^1 11_0^1 12_0^1$  transitions, respectively. The  $11_0^1 12_0^1$  shift further aligns well with the  $1113\text{ cm}^{-1}$  feature in the LIF spectra of Ref. 51 that was re-assigned to the  $\nu_{11} + \nu_{12}$  combination band by Thomas *et al.*<sup>46</sup>

#### **$\nu_4$ IR-cryo-SEVI spectrum**

Because of the excellent agreement between the experimental difference spectrum (Figure 3d) and the FC simulation (Figure 3e), including only transitions that originate from the  $\nu_4$  zeroth-order

state, all labeled features can be unambiguously identified. The assignment is shown in Table 2. Overall, the  $\nu_4$  IR-cryo-SEVI spectrum provides a simple case in which the initially prepared state is well-characterized by excitation of this vibration with negligible anharmonic coupling to other vibrational levels. This observation is consistent with the VPT2 calculations, which do not identify any strong resonance interactions.

As mentioned in Section 4.1, peak B1 at  $13167\text{ cm}^{-1}$  marks the onset of the  $\nu_4$  spectrum and is assigned to the  $4_1^0$  transition. The shift of the  $4_1^0$  transition with respect to the vibrational origin of  $-1554(16)\text{ cm}^{-1}$ , reflecting the vibrational energy of the anion after IR pre-excitation, gives another measurement of the  $\nu_4$  frequency in the anion that is consistent with the band center estimated from the corresponding IR action spectrum at  $\sim 1567\text{ cm}^{-1}$  (see Figure S7b). The spacing between peaks B1, B2 and B4 is consistent with a progression in the  $\nu_9$  mode ( $4_1^0$ ,  $4_1^0 9_0^1$  and  $4_1^0 9_0^2$ ) that is also clearly seen in the FC simulation. B6, which lies close to the vibrational origin but is still partially resolved, is assigned to the  $4_1^1$  sequence band. Overall, these transitions terminate in neutral levels that are also observed in the ground state spectrum but are now shifted to lower eBE due to initial excitation of the  $\nu_4$  mode in the anion.

The above-mentioned peaks, as well as peaks B8-B12, mainly show activity in the neutral  $\nu_4$ ,  $\nu_7$  and  $\nu_9$  vibrations, which are already FC-active starting from the vibrational ground state. The remaining peaks (B3, B5 and B7) show FC activity in the  $\nu_5$  and  $\nu_8$  modes, which are not accessible from the vibrational ground state and become active following  $\nu_4$  excitation through Duschinsky rotation. This effect results from the differences between the normal coordinates that describe the  $\nu_4$  mode in the anion and neutral.<sup>72</sup> More specifically, when the normal coordinate that describes the  $\nu_4$  mode of the anion is projected onto the normal modes of the neutral, it not only contains contributions of the neutral  $\nu_4$  mode but also of the neutral  $\nu_5$  and  $\nu_8$  modes. Based on the FC simulation, peak B3 is assigned to the  $4_1^0 8_0^1$  transition and leads to an estimate of  $954(10)\text{ cm}^{-1}$  for the  $\nu_8$  fundamental. Peaks B5 and B7 are assigned to  $4_1^0 5_0^1$  and  $4_1^0 5_0^1 9_0^1$  which yields a  $\nu_5$  fundamental frequency of  $1395(11)\text{ cm}^{-1}$ , in close agreement with the calculated anharmonic VPT2 frequency of  $1409\text{ cm}^{-1}$ . However, this value strongly deviates from the  $\nu_5$  frequency reported in Ref. 51 ( $1486\text{ cm}^{-1}$ ); this discrepancy will be discussed in Section 5.

### **$\nu_3$ IR-cryo-SEVI spectrum**



As mentioned earlier, the harmonic FC spectrum of the zeroth-order  $\nu_3$  state (Figure 4c) is not sufficient to explain the large number of observed transitions in Figure 4b. First, we will address the transitions below the vibrational origin, which are caused by anharmonic coupling of the  $\nu_3$  fundamental in the anion. We then discuss the origin of the quartet features above the vibrational origin that are mainly caused by anharmonic coupling of  $\nu_3$  within the neutral.

The features below the vibrational origin appear in a region where hot band transitions that involve lower frequency vibrations would normally be expected. However, the “hot bands” seen in the IR-cryo-SEVI spectrum cannot originate from thermally populated vibrational states as the molecules are selectively excited with a narrow  $\sim 3 \text{ cm}^{-1}$  bandwidth and no hot bands are observed in the ground state cryo-SEVI spectrum. At the same time, the laser bandwidth is sufficiently narrow to only excite a single vibrational level instead of multiple eigenstates within the  $3_1$  resonant space of the anion. We thus interpret the additional transitions below the vibrational origin as contributions of various zeroth-order states that are mixed into the wavefunction of the nominal  $\nu_3$  eigenstate in the anion through anharmonic coupling. Inspection of the squared mixing coefficients,  $|c_j''|^2$ , obtained from diagonalization of the anion coupling matrix (Tables S3 and S4), indeed shows a significant contribution of the  $\nu_4 + \nu_8$  zeroth-order state (28%) next to that of the  $\nu_3$  zeroth-order state (69%). Another small contribution comes from the  $2\nu_6$  overtone (2%). Figure 5 illustrates how contributions from such zeroth-order dark states can enable transitions that would not be FC-allowed from the  $\nu_3$  zeroth-order bright state.

Figure 6a shows the anharmonic FC spectrum evaluated using eq 6, in which anharmonic coupling in the anion is considered while assuming that no neutral anharmonic coupling is present within the plotted region below the vibrational origin. Overall, the simulated intensities and frequencies of FC-allowed transitions (dotted line in Figure 6a) are in good agreement with the experimentally observed transitions below the vibrational origin (Figure 6b). See Section S1.2 and Table S5 for details on how the eBEs were calculated. The stick spectrum in Figure 6a thus allows us to confidently assign many of the experimentally observed peaks (c1-c19 in Figure 6b) to transitions from the nominal  $3_1$  level in the anion into different neutral states, as shown in Table 3. These neutral states all have low vibrational energy and thus are expected to exhibit negligible anharmonic coupling, justifying the use of eq 6.

Although the calculated anharmonic FC factors are extremely sensitive to the exact contributions of different anion zeroth-order states, most transitions can still be assigned to a nominal anion zeroth-order state by inspection of the FC spectra obtained for the individual anion zeroth-order states that contribute to the nominal  $\nu_3$  eigenstate, weighted by the square of the corresponding expansion coefficients. These spectra will be referred to as “weighted FC spectra”. This approach corresponds to neglecting the cross-terms between different anion zeroth-order states in eq 6 when evaluating the FC spectrum and is described in Section S2. When one of the contributions to the weighted FC spectrum, shown in Figure S8, anticipates a peak in the spectrum, the nominal anion zeroth-order state is also indicated in Table 3 and above the anharmonic FC simulation in Figure 6a by colored combs. In particular, coupling to the  $\nu_4 + \nu_8$  zeroth-order state explains most of the spectrum below the vibrational origin. However, some observed peaks, such as c1, c4 and c9, are not reproduced by the FC simulation and are likely attributed to an additional anharmonic resonance that is not captured by the present model. Discrepancies between the experimental and simulated spectra may further arise from the fact that harmonic zeroth-order states are used to approximate the deperturbed basis states in eq 6.

Figure 7b shows the experimentally observed structure in the vicinity of the expected  $3_1^1$  transition. Here, the intense quartet cannot be explained by the FC spectra based only on coupling amongst the anion zeroth-order states. We therefore argue that at least some of the features C1a-d are caused by strong anharmonic splitting of the neutral  $3^1$  level. The resonant coupling space of the neutral  $\nu_3$  mode thus needs to be explicitly considered in the anharmonic FC simulations. This will be discussed in detail for the splitting of the  $3_1^1$  transition, but the same explanation should also hold for the splitting of the  $3_1^1 9_0^1$ ,  $3_1^1 9_0^2$  and  $3_1^1 7_0^1$  transitions if we assume that the  $\nu_7$  and  $\nu_9$  modes merely act as spectator modes.

The FC simulation in Figure 7a, which includes anharmonic coupling both within the anion and neutral according to eq 5, is in good agreement with the experimental spectrum in Figure 7b. The convolution of the simulated spectrum (dotted line in Figure 7a) shows five peaks, four of which have similar positions and relative intensities as the experiment (Figure 7b). It should again be noted that the exact values of the anharmonic FC factors are very sensitive to the anion zeroth-order state contributions. Also here, “weighted FC spectra” (Section S2 and Figure S9) allow us to nominally assign peaks C1a-d to different anion zeroth-order states, as indicated by the colored combs above the anharmonic FC simulation (stick spectrum in Figure 7a). Almost all transitions

that contribute to peaks C1a-c can be nominally assigned to the  $\nu_3$  zeroth-order anion state (red), whereas only a small contribution to peak C1c comes from the  $\nu_4 + \nu_8$  zeroth-order state (blue). Those peaks are thus mainly caused by anharmonic splitting of the neutral  $3^1$  level. However, peak C1d is caused by transitions that originate from the  $\nu_4 + \nu_8$  zeroth-order state.

Unfortunately, the vibrational states in the  $3^1$  resonant space are so strongly mixed that it is difficult to make nominal state assignments. Only the intense peak at  $2723\text{ cm}^{-1}$  in Figure 7a, which contributes to C1a, has clearly dominant  $2\nu_6$  character. The other states that contribute to peaks C1a-C1c mostly show contributions from several resonant neutral states that can be found in the coefficient matrix in the SI in a separate spreadsheet. As no definite assignments to nominal states can be given, we will collectively refer to peaks C1a-C1c as a  $3^1$  polyad in Table 3.<sup>78,79</sup> The same splitting due to the polyad structure is also expected for the other transitions,  $3_1^1 9_0^1$ ,  $3_1^1 9_0^2$  and  $3_1^1 7_0^1$ . The corresponding peaks will therefore be assigned to  $3^1 9^1$ ,  $3^1 9^2$  and  $3^1 7^1$  polyads.

## 5. Discussion

The fundamental frequencies of the vinoxy radical extracted from the cryo-SEVI and IR-cryo-SEVI spectra are summarized in Table 4, together with the calculated VPT2 frequencies and other experimental values from the literature. For most frequencies, the agreement with the most recent experimental data is within our estimated error limits. The  $\nu_5$  frequency of  $1395(11)\text{ cm}^{-1}$  determined in this work, on the other hand, clearly deviates from the best estimate of  $1486\text{ cm}^{-1}$  obtained through LIF spectroscopy.<sup>49,51</sup> Also the splitting of the  $3_1^1$  peak into three features has not been previously observed. However, the frequency of  $2835(18)\text{ cm}^{-1}$ , extracted from the central peak C1b, is consistent with the band center determined in Ref. 53, the only other report of the  $\nu_3$  frequency.

The comparison between the  $\nu_4$  IR-cryo-SEVI spectrum and the FC simulation in Figure 3 allows us to unambiguously determine the  $\nu_5$  frequency from peaks B5 and B7. In addition, our VPT2 frequency calculations including anharmonic resonances predict a value of  $1409\text{ cm}^{-1}$ , which lies almost within the error of our experimental value. This calculated value is also in line with the more recent MRCISD calculation by Yamaguchi *et al.*,<sup>52</sup> who reported a scaled harmonic frequency of  $1441\text{ cm}^{-1}$ , and anharmonic VPT2 calculations by Thomas *et al.*<sup>46</sup> at the B3LYP/aug-cc-pVTZ level of theory, providing a value of  $1392\text{ cm}^{-1}$ . The discrepancy between our value of

1395(11)  $\text{cm}^{-1}$  for the  $\nu_5$  fundamental frequency and other measurements therefore most likely results from previous assignments being based on harmonic frequency values.

Considering how well our calculated VPT2 frequencies agree with all the other fundamental frequencies, it is likely that the  $\nu_5$  fundamental frequency and its resonances with nearby vibrational states are also described correctly. This allows us to identify the origin of its anharmonic shift. The resonant space of the  $\nu_5$  mode in the neutral shows a strong Fermi resonance between the  $\nu_5$  fundamental and the  $2\nu_{11}$  overtone, with a coupling matrix element of  $38.3 \text{ cm}^{-1}$ , along with other weaker resonances (see Table S6). This Fermi resonance results in two calculated levels at 1409 and  $1494 \text{ cm}^{-1}$  with dominant  $\nu_5$  and  $2\nu_{11}$  character, respectively (Table S7). The photodetachment transition into the upper level, expected at an eBE of  $14662 \text{ cm}^{-1}$ , cannot be clearly identified in the IR-cryo-SEVI spectrum because it would partially overlap with the  $4_1^1$  feature and the depleted vibrational origin. We speculate that the  $1486 \text{ cm}^{-1}$  level, which was assigned to the  $\nu_5$  fundamental by Brock and Rohlfiing,<sup>51</sup> belongs to the upper level of the Fermi resonance pair. On the other hand, no transition for the lower level with comparable intensity is reported at a shift of  $\sim 1395 \text{ cm}^{-1}$  in Ref. 51.

We now discuss the strong anharmonic splitting within the  $3^1$  polyad of the vinoxy radical, with peaks at 2737(22), 2835(18) and  $2910(12) \text{ cm}^{-1}$  (C1a-C1c). The  $\nu_3$  mode shows a comparatively isolated vibration, mainly involving motion of the C-H bond, while structural changes during photodetachment from the vibrational ground state primarily occur within the C-C-O backbone (see Table S1). The same is true for  $\tilde{B}^2A'' - \tilde{X}^2A''$  fluorescence experiments where the C-H bond distances remain almost unchanged in the  $\tilde{B}$  state.<sup>34, 36, 38, 52</sup> The  $\nu_3$  mode as well as the other two C-H stretching vibrations are therefore not FC-active in any of those experiments and it should generally be easier to observe them with IR spectroscopy. There, a comparable redistribution of the  $\nu_3$  oscillator strength across different neutral vibrations as in the red stick spectrum in Figure S9b would be expected due to anharmonic coupling. However, only two such IR absorption studies exist to the best of our knowledge. In an argon matrix isolation study, a germanium filter with a cutoff of  $\sim 2000 \text{ cm}^{-1}$  was used to avoid changes within the sample while exposing it to the IR radiation, which prevented measurements of the C-H stretching vibrations.<sup>42</sup> In the second experiment by Utkin *et al.*,<sup>53</sup> a high-resolution gas phase study, the observation of transitions at 2737(22) and  $2910(12) \text{ cm}^{-1}$  (C1a and C1c, respectively) should have in principle been possible but the authors only reported the center peak at  $2827.91259(3) \text{ cm}^{-1}$  (C1b). Their data for jet-cooled

vinoxy has only been collected in the 2809-2860  $\text{cm}^{-1}$  range, where rovibrational transitions from the two coupled vibrations would likely not be observed. Their room temperature spectrum was measured over a larger range of 2754-2894  $\text{cm}^{-1}$  but is also more congested, which might explain why the anharmonic resonances could not be identified. On the other hand, Utkin *et al.* did note that perturbations with nearby vibrational levels exist and that many transitions originating from about half of the observed  $K'_a$  levels seem to be systematically perturbed, which might be a result of the strong anharmonic coupling reported in the present work.

The high frequency of the excited  $\nu_3$  mode in the anion and neutral, associated with a higher vibrational state density,<sup>80</sup> facilitates anharmonic coupling in notable contrast to excitation of the lower frequency  $\nu_4$  mode. Despite the strong coupling present in the  $\nu_3$  IR-cryo-SEVI spectra, anharmonic FC simulations enable us to identify specific zeroth-order dark state contributions to the nominal  $\nu_3$  mode in the anion (Figure 6) as well as vibrational eigenstates with  $\nu_3$  character in the neutral (Figure 7). Therefore, IR-cryo-SEVI has features in common with other spectrally resolved techniques that are used to probe anharmonic coupling in electronic ground states.<sup>22-24</sup> It is worth noting that in IR-cryo-SEVI the information on coupling within the anion and neutral ground states is spectrally separated into two eBE regions. Further note that we based our current analysis solely on vibrational coupling and did not consider the effect of rovibrational structure, which can potentially alter the relative intensities of contributions from the  $\nu_3$  zeroth-order bright state and other zeroth-order dark states. A similar, temperature-dependent effect is, for example, seen in IR fluorescence experiments that probe anharmonic coupling of other C-H stretching vibrations.<sup>81, 82</sup>

The observation of the  $\nu_3$ ,  $\nu_5$  and  $\nu_8$  modes in the neutral, which are not accessible from the anion ground state, highlights another benefit of the IR-cryo-SEVI technique. As explained earlier, excitation of the  $\nu_4$  mode, which shares the same symmetry as the vibrational ground state, gives rise to distinctive FC activity in the  $\nu_5$  and  $\nu_8$  modes due to Duschinsky mixing,<sup>72</sup> in addition to activity in the  $\nu_4$ ,  $\nu_7$  and  $\nu_9$  modes seen in the “IR off” spectrum. Besides this approach of accessing otherwise inactive neutral vibrations through the Duschinsky effect, the excitation of modes of different symmetry to access non-totally symmetric modes in the neutral will be another promising direction for future experiments. Such experiments could, for example, include the isomerization dynamics of vinylidene to acetylene, which mainly involves the  $\nu_5$  and  $\nu_6$  modes of neutral

vinylidene, where both modes are of  $b_2$  symmetry and could only be observed as weak transitions due to Herzberg-Teller coupling in previous cryo-SEVI studies.<sup>83</sup>

Finally, it is worth noting that the approach taken here to simulate the IR-cryo-SEVI spectrum is straightforward, general, and computationally efficient. It is built off of the harmonic FC treatment that is typically used to analyze spectra with transitions originating from the vibrational ground state of the anion. In this approach, vibrational perturbation theory is used to develop a basis of states that are nearly degenerate with the state of interest along with their deperturbed energies. This allows for analysis of the spectrum in terms of this limited vibrational basis, where the associated vibrational wave functions are treated within the harmonic approximation. With this in place, the IR-cryo-SEVI spectrum may be modeled using the FC factors evaluated based on the harmonic zeroth-order states. While similar approaches to the evaluation of anharmonic FC factors have been previously used based on anharmonic wavefunctions obtained from variational calculations,<sup>74,75</sup> those methods are computationally expensive for large molecules. For covalently bound systems like vinoxide or vinoxy where vibrational perturbation theory is generally effective, it provides a simple approach for detangling the complicated spectral effects of anharmonic coupling in both the anionic and neutral species.

## 6. Conclusion

The presented high-resolution photoelectron spectra of vibrationally excited vinoxide anions show the first application of IR-cryo-SEVI to a polyatomic molecule. The IR-cryo-SEVI spectrum of vinoxide excited along the C-O stretching mode ( $\nu_4$ ) is well described within the harmonic approximation, indicating that anharmonic coupling in the anion is negligible for that mode. Furthermore, transitions into the  $\nu_5$  and  $\nu_8$  modes in the neutral are observed after  $\nu_4$  excitation, which are not accessible from the vibrational ground state, allowing us to extract their fundamental frequencies. For the  $\nu_5$  mode, existing literature values strongly deviate from our measurement at  $1395(11) \text{ cm}^{-1}$ . This deviation is explained by a strong Fermi resonance between the  $\nu_5$  fundamental and the  $2\nu_{11}$  overtone, resulting in a lower level at  $1395 \text{ cm}^{-1}$  and an upper level expected near  $1490 \text{ cm}^{-1}$ . The latter feature is not explicitly observed in our experiment but lies close to the value reported in previous work.

The IR-cryo-SEVI spectrum of vinoxide excited along the isolated C-H stretching mode ( $\nu_3$ ) is more complex and explained by anharmonic coupling of the  $\nu_3$  fundamental with other near-

degenerate vibrations in the anion and the neutral. The measured  $\nu_3$  IR-cryo-SEVI spectra are qualitatively reproduced by anharmonic Franck-Condon simulations. The effects of anharmonicity are included through nearly-degenerate vibrational perturbation theory and the resultant nearly-degenerate states serve as a basis within the context of anharmonic Franck-Condon simulations. The analysis shows that many observed “hot band” transitions can be explained by anharmonic coupling within the anion electronic ground state. Furthermore, a polyad comprising three distinct features at 2737(22), 2835(18) and 2910(12)  $\text{cm}^{-1}$  instead of a single feature are reported for the  $\nu_3$  fundamental in the neutral, indicating strong anharmonic resonances that are also reproduced by the Franck-Condon simulations.

Overall, the reported IR-cryo-SEVI and ground state cryo-SEVI measurements presented here allow us to measure nine out of the twelve fundamental frequencies of the vinyloxy radical (except for  $\nu_1$ ,  $\nu_2$  and  $\nu_{10}$ ) with a single experimental setup. In addition, the vibrational frequencies of the  $\nu_4$  and  $\nu_3$  fundamentals in the anion are found near 1567 and 2540  $\text{cm}^{-1}$  using IR-cryo-SEVI as an action spectroscopy technique. The well-resolved IR-cryo-SEVI spectra—especially considering the strong coupling within the  $\nu_3$  mode—suggest that many more applications to other polyatomic systems are now possible.

## Acknowledgments

The research at UC Berkeley was funded by the Air Force Office of Scientific Research (AFOSR) under Grant No. FA9550-19-1-0051 and the AFOSR Defense University Research Instrumentation Program under Grant No. FA9550-19-1-0139, DEF. A.B.M and M.A.B. acknowledge support from the Chemistry Division of the National Science Foundation (Grant No. CHE-2154126). This work was funded by Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) within project 430942176 (K.R.A.). J.A.L. thanks the Alexander von Humboldt Foundation for a Feodor Lynen Research Fellowship. M.C.B. thanks the Army Research Office for a National Defense Science and Engineering Graduate fellowship. M.G. gratefully acknowledges a doctoral scholarship from the Studienstiftung des deutschen Volkes (German Academic Scholarship Foundation). We thank Anna Krylov and Paweł Wójcik for including the option to calculate Franck-Condon spectra of specific vibrational anion states in the most recent version of ezFCF.

## Supporting Information

Additional experimental and theoretical details (PDF): details of the anharmonic Franck-Condon simulations (Section S1), a description of the “weighted FC spectra” method (Section S2), experimental setup (Figure S1), normal modes (Figures S2 and S3), FC simulations for different frequency shifts (Figures S4 and S5), anisotropy parameters (Figure S6), infrared action spectra (Figure S7), weighted FC spectra (Figures S8 and S9), Optimized geometries in valence (Table S1) and Cartesian coordinates (Table S2), anion  $\nu_3$  coupling and coefficient matrices (Tables S3 and S4), fundamental frequencies used in eBE calculations for the  $\nu_3$  simulations (Table S5), neutral  $\nu_5$  coupling and coefficient matrices (Tables S6 and S7).

Coupling and coefficient matrices for the anion and neutral  $\nu_3$  fundamental and neutral  $\nu_5$  fundamental (XLS).

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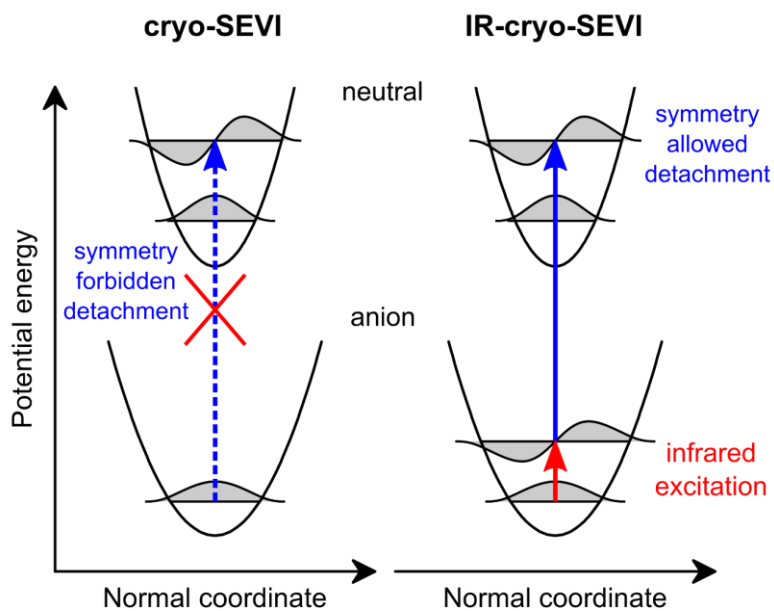
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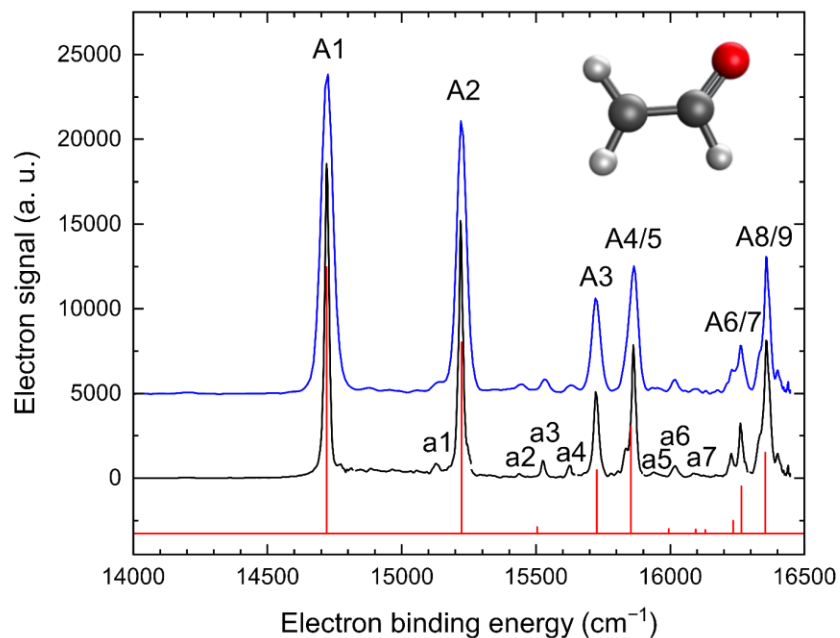
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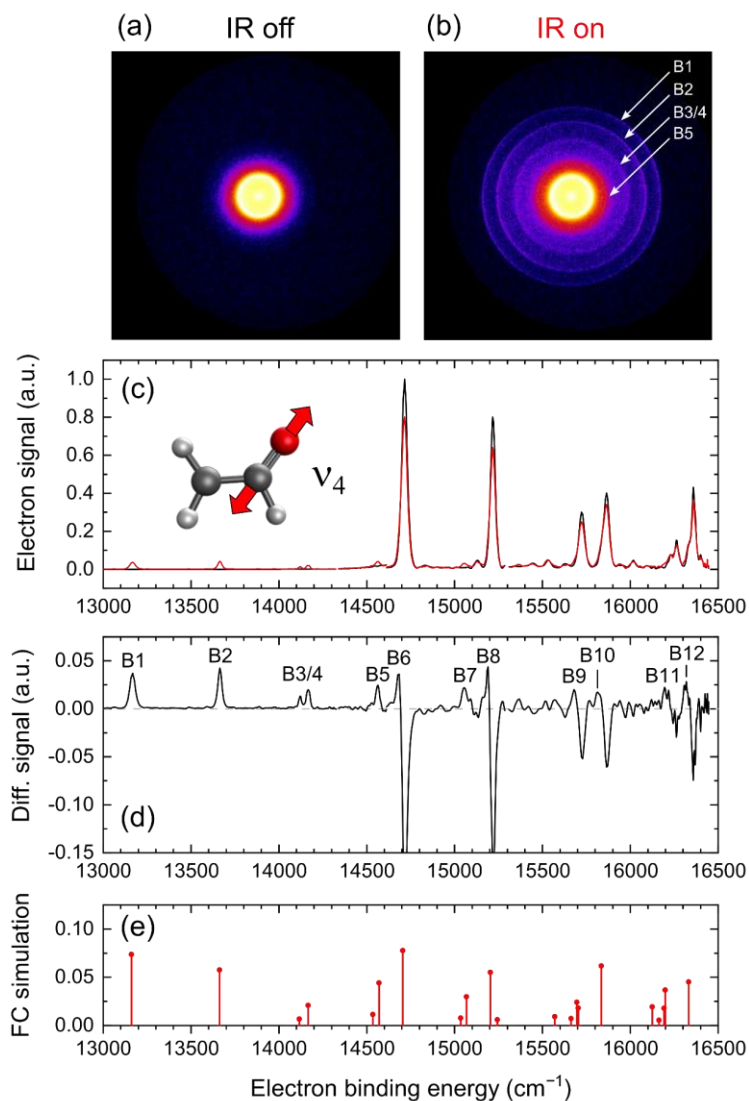
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**Figure 1.** Schematic illustration of how infrared excitation of a non-totally symmetric anion vibration results in new vibrational transitions becoming accessible via photodetachment. Red arrows indicate IR excitation in the anion and blue arrows indicate photodetachment.



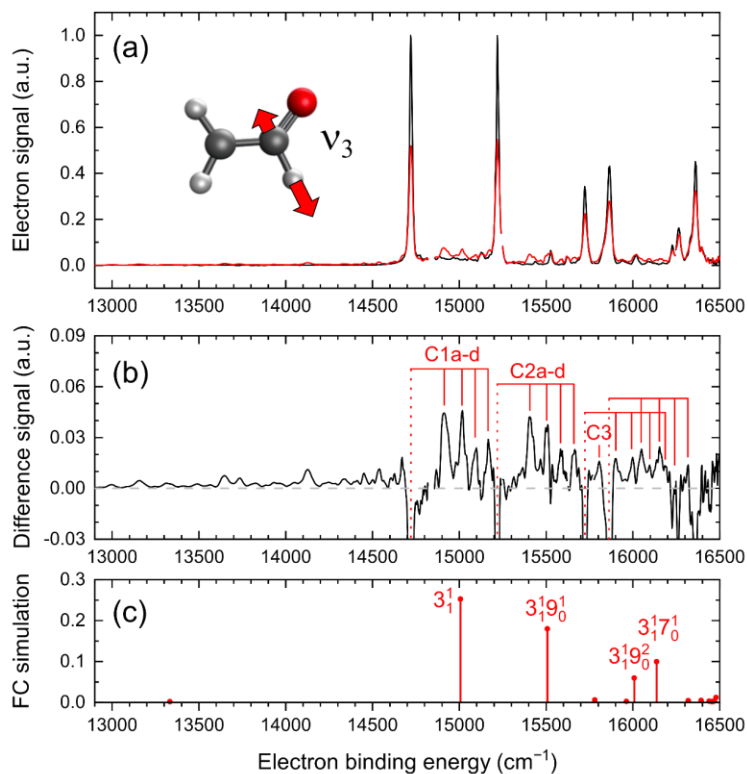
**Figure 2.** Top trace (blue curve): Overview photoelectron spectrum of the vinoxide anion taken at a detachment photon energy of  $16446 \text{ cm}^{-1}$  without IR excitation. Center trace (black curves): Corresponding high-resolution spectra taken at several lower photon energies and scaled to reflect the intensities in the overview spectrum. Bottom trace (red curve): Harmonic Franck-Condon simulation for detachment from the vibrational ground state of the anion (see Section 3.2 for details).



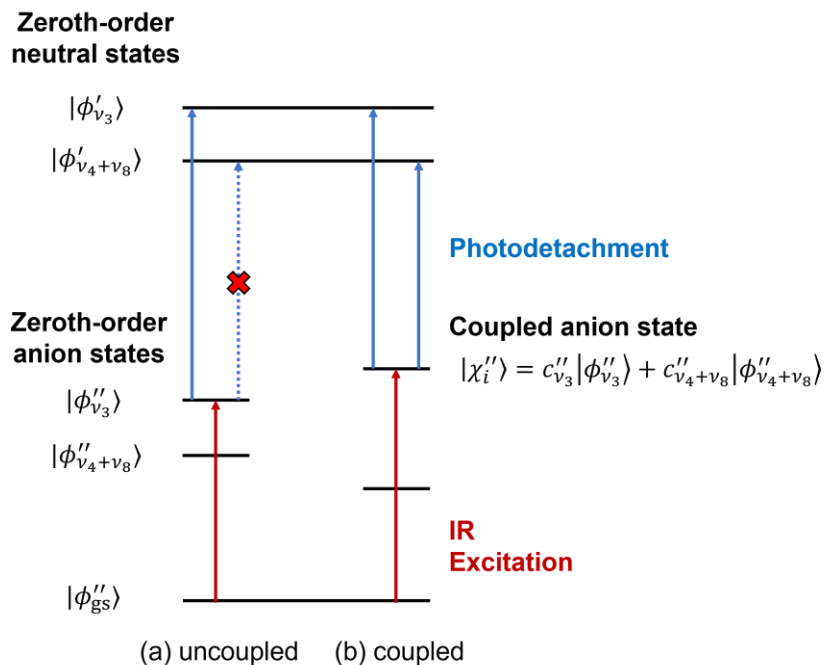
**Figure 3.** (a) Accumulated velocity-map image obtained from experimental cycles where the IR laser is not firing (“IR off”) at a photodetachment energy of  $14810 \text{ cm}^{-1}$ . (b) Simultaneously acquired image for the cycles where the IR laser vibrationally excited the vinoxide anions *via* the  $\nu_4$  fundamental frequency at  $1570 \text{ cm}^{-1}$  (“IR on”). Both images share the same logarithmic intensity scale to emphasize additional features upon IR excitation, which are indicated by arrows and labels. (c) Concatenated high-resolution spectra under “IR off” (black curves) and “IR on” (red curves) conditions. The IR laser was fixed near the  $\nu_4$  fundamental frequency at  $1570 \text{ cm}^{-1}$ . All high-resolution pairs are scaled such that the peak intensity of the vibrational origin in the “IR off” spectrum is normalized to 1, except for one scan taken with a detachment energy below the



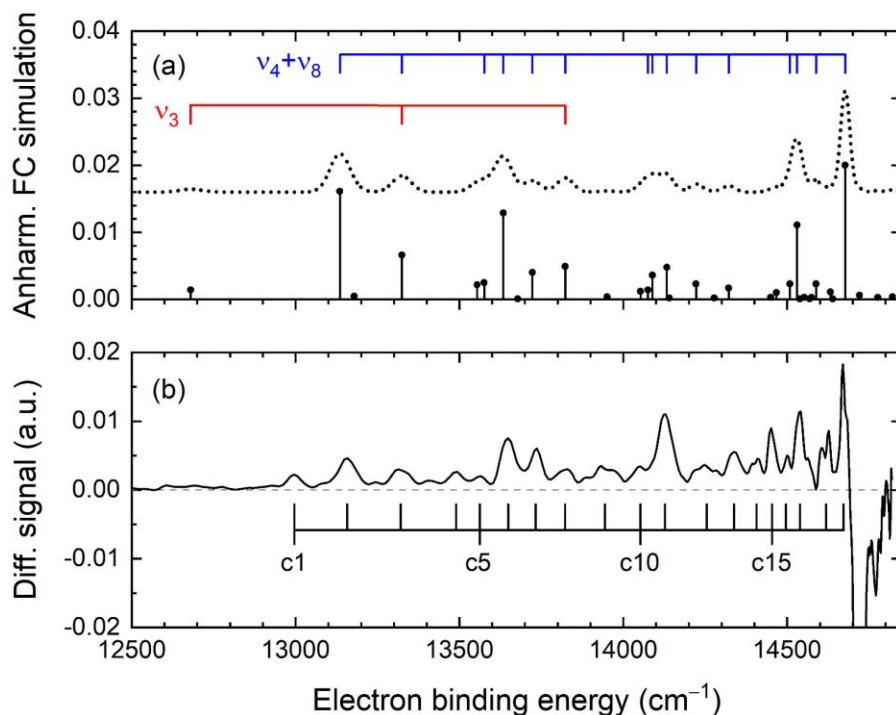
vibrational origin. In the latter case, the spectrum is scaled such that the intensity of the  $13167\text{ cm}^{-1}$  feature agrees with that of the scan taken at the next higher detachment energy. (d) Corresponding difference spectra for the high-resolution spectra shown in panel c (“IR on” – “IR off”) including peak labels. Assignments are shown in Table 2. (e) Harmonic Franck-Condon simulation for photodetachment from vinoxide excited *via* the  $\nu_4$  fundamental. Transitions originating from the vibrational ground state in the anion are not shown.



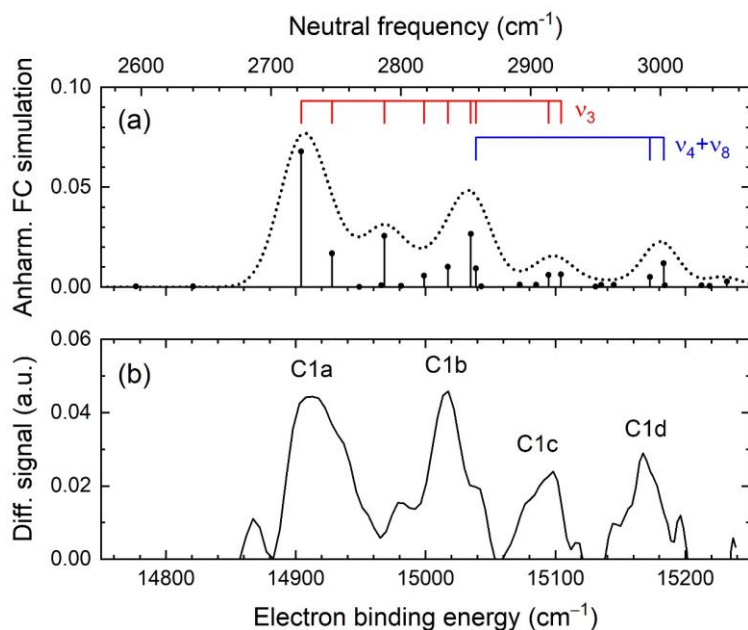
**Figure 4.** (a) Concatenated high-resolution spectra under “IR off” (black curves) and “IR on” (red curves) conditions for IR laser excitation *via* the  $\nu_3$  fundamental frequency at 2546 cm<sup>-1</sup>. All high-resolution pairs are scaled such that the peak intensity of the vibrational origin in the “IR off” spectrum is normalized to 1. (b) Corresponding difference spectra for the high-resolution spectra shown in panel a (“IR on” – “IR off”). Combs and labels indicate groups of four peaks that are observed for each expected transition shown in panel c. (c) Harmonic FC simulation for transitions originating from the zeroth-order  $\nu_3$  state in the anion, using deperturbed VPT2 frequencies without considering anharmonic resonances to calculate the electron binding energies.



**Figure 5.** Schematic energy level diagram showing how additional photodetachment transitions arise due to anharmonic coupling of the  $\nu_3$  mode with other vibrational levels. Anion and neutral zeroth-order states for the uncoupled case are shown on the left (a) and the excited anharmonically coupled eigenstate in the anion is shown on the right (b). IR excitation is shown by red arrows and detachment transitions are shown by blue arrows. The dashed arrow indicates a non-FC allowed transition. Note that only two zeroth-order states ( $\nu_3$  and  $\nu_4 + \nu_8$ ) with the largest contributions to the coupled anion state are shown for clarity. Anharmonic coupling within the neutral is also neglected in this scheme and neutral zeroth-order states are shown instead for both cases.



**Figure 6.** (a) Black stick spectrum shows the anharmonic Franck-Condon simulation for vinoxide excited *via* the  $\nu_3$  fundamental below the vibrational origin. Anharmonic FC factors are calculated according to eq 6, including all anion zeroth-order states, but assuming no anharmonic coupling between neutral states. Dotted line shows a convolution of the stick spectrum, offset and scaled by an arbitrary scaling factor, using an eKE-dependent linewidth as described in Section S1.3. Colored combs indicate transitions that can nominally be assigned to the  $\nu_4 + \nu_8$  (blue) and  $\nu_3$  (red) anion zeroth-order states. Note that the transitions explaining peaks c3 and c8 show contributions from both the  $\nu_4 + \nu_8$  and  $\nu_3$  zeroth-order states. (b) Experimental low eBE region of the  $\nu_3$  IR-cryo-SEVI difference spectrum below the vibrational origin based on the corresponding high-resolution scan from Figure 4b, which was measured at a photon energy of 14848 cm<sup>-1</sup>. Observed peaks are indicated by the combs and labels. Corresponding peak assignment can be found in Table 3.



**Figure 7.** (a) Black stick spectrum shows the anharmonic Franck-Condon simulation for vinoxide excited *via* the  $\nu_3$  fundamental in the eBE region near the expected  $3_1^1$  transition, calculated according to eq 5 in which anharmonic coupling for both the anion and neutral  $\nu_3$  modes is included. Dotted line shows a convolution of the stick spectrum, scaled by an arbitrary scaling factor and using an eKE-dependent linewidth as described in Section S1.3. Colored combs indicate transitions that can nominally be assigned to the  $\nu_3$  (red) and  $\nu_4 + \nu_8$  (blue) anion zeroth-order states. Neutral frequencies shown at the top are related to the eBE by a shift of  $-EA + \nu_{3,\text{anion}} = -12181 \text{ cm}^{-1}$ , where the electron affinity is  $EA = 14721 \text{ cm}^{-1}$  and the anion frequency is estimated as  $\nu_{3,\text{anion}} = 2540 \text{ cm}^{-1}$ . (b) Experimental difference spectrum near the expected  $3_1^1$  transition based on the corresponding high-resolution scan from Figure 4b, which was measured at a photon energy of  $15290 \text{ cm}^{-1}$ .

**Table 1.** Electron Binding Energies (eBE) and Assignments for the Ground State cryo-SEVI Spectrum.

Peak	eBE (cm <sup>-1</sup> ) <sup>a</sup>	Assignment	Shift to 0 <sub>0</sub> <sup>0</sup>	Shift to 9 <sub>0</sub> <sup>1</sup>
A1	14721(8)	0 <sub>0</sub> <sup>0</sup>	0	
a1	15129(10)	12 <sub>0</sub> <sup>1</sup>	408	
A2	15220(8)	9 <sub>0</sub> <sup>1</sup>	499	0
a2	15438(6)	11 <sub>0</sub> <sup>1</sup>	717	218
a3	15527(7)	12 <sub>0</sub> <sup>2</sup>	805	306
a4	15625(8)	9 <sub>0</sub> <sup>1</sup> 12 <sub>0</sub> <sup>1</sup>	904	405
A3	15724(10)	9 <sub>0</sub> <sup>2</sup>	1003	504
A4	15835(9)	11 <sub>0</sub> <sup>1</sup> 12 <sub>0</sub> <sup>1b</sup>	1114	615
A5	15864(8)	7 <sub>0</sub> <sup>1</sup>	1143	644
a5	15941(17)	12 <sub>0</sub> <sup>3</sup>	1220	721
a6	16018(11)	9 <sub>0</sub> <sup>1</sup> 12 <sub>2</sub> <sup>0</sup>	1297	798
a7	16094(15)	6 <sub>0</sub> <sup>1</sup>	1373	874
A6	16228(8)	9 <sub>0</sub> <sup>3</sup>	1507	1008
A7	16263(9)	4 <sub>0</sub> <sup>1</sup>	1542	1043
A8	16330(8)	9 <sub>0</sub> <sup>1</sup> 11 <sub>0</sub> <sup>1</sup> 12 <sub>0</sub> <sup>1b</sup>	1609	1110
A9	16360(11)	7 <sub>0</sub> <sup>1</sup> 9 <sub>0</sub> <sup>1</sup>	1639	1140

<sup>a</sup> Electron binding energies are determined from Gaussian fits to the highest-resolution scan for that peak and the uncertainties in parentheses are estimated as  $1\sigma$ , based on the widths of the Gaussian fits.

<sup>b</sup> Assignment based on the sum of the  $\nu_{11}$  and  $\nu_{12}$  fundamentals. The resulting estimate of 1114(9) cm<sup>-1</sup> for the  $\nu_{11} + \nu_{12}$  combination also agrees well with the assignment of Thomas *et al.*<sup>46</sup>

**Table 2.** Electron Binding Energies (eBE) and Assignments for the IR-cryo-SEVI Spectrum of Vinoxide Excited Along the  $\nu_4$  Vibration.

Peak	eBE (cm <sup>-1</sup> ) <sup>a</sup>	Assignment	Shift to $4_1^0$
B1	13167(16)	$4_1^0$	0
B2	13664(12)	$4_1^0 9_0^1$	498
B3	14121(10)	$4_1^0 8_0^1$	954
B4	14166(11)	$4_1^0 9_0^2$	999
B5	14562(11)	$4_1^0 5_0^1$	1395
B6	14701(16) <sup>b</sup>	$4_1^1$	1534
B7	15055(15)	$4_1^0 5_0^1 9_0^1$	1889
B8	15206(16) <sup>b</sup>	$4_1^1 9_0^1$	2040
B9	15704(24) <sup>b</sup>	$4_1^0 5_0^1 7_0^1$ $4_1^1 9_0^2$	2537
B10	15816(13)	$4_1^1 7_0^1$	2649
B11	16202(18)	$4_1^2$	3035
B12	16315(12)	$4_1^1 7_0^1 9_0^1$	3148

<sup>a</sup> Electron binding energies are determined from Gaussian fits to the highest-resolution difference spectrum for that peak and the uncertainties in parentheses are estimated as  $1\sigma$  based on the widths of the Gaussian fits unless noted otherwise.

<sup>b</sup> Peak overlaps with another peak that originates from the vibrational ground state. The eBE and its uncertainty are therefore estimated based the eBE difference between the maximum of the positive feature and the minimum of the depleted feature.

**Table 3.** Electron Binding Energies (eBE) and Assignments for the IR-cryo-SEVI Spectrum of Vinoxide Excited Along the  $\nu_3$  Vibration.<sup>a</sup>

Peak	eBE (cm <sup>-1</sup> ) <sup>b</sup>	Assignment (initial zeroth-order state)	Assignment (final eigenstate)	Shift to 3 <sub>1</sub> <sup>0c</sup>
c1	12996(19)	unassigned		815
c2	13157(28)	$\nu_4 + \nu_8$	8 <sup>1</sup>	976
c3	13320(30)	$\nu_4 + \nu_8/\nu_3$	7 <sup>1</sup>	1139
c4	13490(22)	unassigned		1309
c5	13562(20)	2 $\nu_6$	6 <sup>1</sup>	1381
		$\nu_4 + \nu_8$	5 <sup>1</sup>	
c6	13649(24)	$\nu_4 + \nu_8$	8 <sup>1</sup> 9 <sup>1</sup>	1468
c7	13733(21)	$\nu_4 + \nu_8$	4 <sup>1</sup>	1552
c8	13822(28)	$\nu_4 + \nu_8/\nu_3$	7 <sup>1</sup> 9 <sup>1</sup>	1641
c9	13944(35)	unassigned		1763
c10	14052(23)	2 $\nu_6$	6 <sup>1</sup> 9 <sup>1</sup>	1871
		$\nu_4 + \nu_8$	5 <sup>1</sup> 9 <sup>1</sup>	
c11	14127(22)	$\nu_4 + \nu_8$	8 <sup>2</sup>	1946
		$\nu_4 + \nu_8$	8 <sup>1</sup> 9 <sup>2</sup>	
c12	14254(39)	$\nu_4 + \nu_8$	4 <sup>1</sup> 9 <sup>1</sup>	2073
c13	14338(25)	unassigned		2157
c14	14406(16)	unassigned		2225
c15	14454(13)	unassigned		2273
c16	14496(9)	$\nu_4 + \nu_8$	6 <sup>1</sup> 8 <sup>1</sup>	2315
c17	14539(17)	$\nu_4 + \nu_8$	5 <sup>1</sup> 8 <sup>1</sup>	2358
c18	14619(18)	unassigned		2438
c19	14672(9)	$\nu_4 + \nu_8$	4 <sup>1</sup> 8 <sup>1</sup>	2491
C1a	14918(22)	$\nu_3$	3 <sup>1</sup> polyad <sup>d</sup>	2737
C1b	15016(18)	$\nu_3$	3 <sup>1</sup> polyad <sup>d</sup>	2835
C1c	15091(12)	$\nu_3$	3 <sup>1</sup> polyad <sup>d</sup>	2910
C1d	15169(14)	$\nu_4 + \nu_8$	4 <sup>1</sup> 8 <sup>1</sup> 9 <sup>1</sup>	2988
C2a	15410(16)	$\nu_3$	3 <sup>1</sup> 9 <sup>1</sup> polyad <sup>d</sup>	3229
C2b	15503(9)	$\nu_3$	3 <sup>1</sup> 9 <sup>1</sup> polyad <sup>d</sup>	3322
C2c	15585(10)	$\nu_3$	3 <sup>1</sup> 9 <sup>1</sup> polyad <sup>d</sup>	3404
C2d	15663(15)	$\nu_4 + \nu_8$	4 <sup>1</sup> 8 <sup>1</sup> 9 <sup>2</sup>	3482
		$\nu_4 + \nu_8$	5 <sup>1</sup> 7 <sup>1</sup> 8 <sup>1</sup>	
C3	15804(11)	$\nu_4 + \nu_8$	4 <sup>1</sup> 8 <sup>1</sup> 7 <sup>1</sup>	3623

<sup>a</sup> Assignments are given for the nominal neutral vibrational states (final) and the zeroth-order anion states (initial) that contribute intensity to transitions into those final states. Initial states separated by a slash indicate that multiple anion zeroth-order states contribute intensity to a transition into the same final state. If multiple transitions into different final states contribute to an observed peak, those are written in different rows.



<sup>b</sup> Electron binding energies are determined from Gaussian fits to the highest-resolution difference spectrum for that peak and the uncertainties in parentheses are estimated as  $1\sigma$  based on the widths of the Gaussian fits.

<sup>c</sup> The  $3_1^0$  transition frequency is estimated as  $EA - \nu_{3,\text{anion}} = 12181 \text{ cm}^{-1}$ , where the electron affinity is  $EA = 14721 \text{ cm}^{-1}$  and the anion frequency is estimated as  $\nu_{3,\text{anion}} = 2540 \text{ cm}^{-1}$ .

<sup>d</sup> See main text for more details on the states involved in the  $3^1$  polyad.

**Table 4.** Fundamental Frequencies of the Vinoxyl Radical Determined in this Work, Calculated VPT2 Frequencies at the B2PLYP-D3/aug-cc-pVTZ Level of Theory, and Most Recent Experimentally Determined Literature Values.

Mode	This work	Source <sup>a</sup>	VPT2	Ref. 46	Ref. 53	Ref. 51	Ref. 36	Ref. 49 <sup>h</sup>
$\nu_1$	-		3147					
$\nu_2$	-		3057					
	2737(22)							
$\nu_3$	2835(18)	$\nu_3$	2806 <sup>b</sup>		2827.91259(3)			
	2910(12)							
$\nu_4$	1542(9)	SEVI	1545 <sup>c</sup>			1543	1528	1540
$\nu_5$	1395(11)	$\nu_4$	1409			1486 <sup>e</sup>		1454
$\nu_6$	1373(15)	SEVI	1374			1366		1361
$\nu_7$	1143(8)	SEVI	1132			1143	1137	1141
$\nu_8$	954(10)	$\nu_4$	955			957		949
$\nu_9$	499(8)	SEVI	501			500	498	498
$\nu_{10}$	-		971			703 <sup>f,g</sup>		
$\nu_{11}$	717(6)	SEVI	728	717 <sup>d</sup>		557 <sup>f,g</sup>		
$\nu_{12}$	408(10)	SEVI	399	402		404 <sup>g</sup>		

<sup>a</sup> Indicates whether the frequency in the present work is extracted from the ground state cryo-SEVI spectrum (SEVI) or the IR-cryo-SEVI spectra ( $\nu_3$  or  $\nu_4$ ).

<sup>b</sup> There is no nominal  $\nu_3$  frequency due to the strong anharmonic coupling involving this mode (see main text). Instead, the deperturbed VPT2 value is reported.

<sup>c</sup> The harmonic frequency of the  $\nu_4$  mode has been shifted by  $-50 \text{ cm}^{-1}$  to achieve this result for the fundamental frequency. Without this shift in the harmonic frequency, the calculated anharmonic fundamental frequency is  $1591 \text{ cm}^{-1}$ .

<sup>d</sup> Based on  $\nu_{11}$  hotband observed in Ref. 46, not their estimate based on the data from Ref. 36.

<sup>e</sup> Potentially the upper level of the  $\nu_5/2\nu_{11}$  Fermi pair (see main text).

<sup>f</sup> These transitions were likely misassigned based on the more recent experiments and calculations.

<sup>g</sup> Estimated as half of the overtone frequency in Ref. 51.

<sup>h</sup> Reanalysis of the LIF data collected before 1990.