# Slow photoelectron velocity-map imaging of cold $C_7^-$ and $C_9^-$

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## Slow photoelectron velocity-map imaging of cold C<sub>7</sub><sup>-</sup> and C<sub>9</sub><sup>-</sup>

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High-resolution anion photoelectron spectra of cryogenically cooled  $C_7^-$  and  $C_9^-$  clusters obtained using slow photoelectron velocity-map imaging are presented, providing insight into the vibronic structure of neutral C<sub>7</sub> and C<sub>9</sub>. These spectra yield accurate measurements of vibrational frequencies for the neutral clusters as well as electron affinities of 3.3517(4) and 3.6766(14) eV for C<sub>7</sub> and C<sub>9</sub>, respectively. In the  $C_7^-$  spectrum, transitions involving the previously unreported  $v_1$  and  $v_2$  symmetric stretching modes, as well as the  $v_9$ ,  $v_{10}$ , and  $v_{11}$  asymmetric bending modes, are assigned. Spin-orbit splitting is observed for several transitions in this spectrum, giving an energy difference of 28(6) cm<sup>-1</sup> between the  ${}^{2}\Pi_{1/2g}$  and  ${}^{2}\Pi_{3/2g}$  spin–orbit levels of the C<sub>7</sub><sup>-</sup> anion. In the spectrum of  $C_9^-$ , transitions involving the previously unreported symmetric stretch  $v_1$  and the asymmetric bend  $v_{11}$  are observed. In both spectra, several features are assigned to Franck-Condon forbidden transitions involving the doubly degenerate  $v_{10}$  and  $v_{11}$  modes of C<sub>7</sub> and the  $v_{13}$  and  $v_{14}$  modes of C<sub>9</sub>. The appearance of these transitions is attributed to Herzberg-Teller coupling between the electronic states of the neutral clusters. Additional FC-forbidden transitions to states previously observed in gasphase infrared experiments are observed and attributed to vibronic coupling between the electronic states of the anion, resulting in non-totally symmetric character in the anion's full vibrational ground state. Finally, consideration of the energy dependence of detachment cross sections and Dyson orbital analyses reveal that addition of more carbon atoms to the linear chain results in photodetachment from delocalized molecular orbitals with increasing nodal structure, leading to threshold photodetachment cross sections that differ considerably from simple symmetry considerations. *Published by* AIP Publishing. https://doi.org/10.1063/1.5054792

### I. INTRODUCTION

Carbon clusters  $(C_n)$  are an extensively researched family of clusters with relevance to interstellar, plasma, and combustion chemistry.<sup>1–5</sup> Spectroscopic signatures of small (n < 10) carbon clusters have been identified in a variety of astrochemical measurements, establishing their presence in comets,<sup>6</sup> the circumstellar shells of carbon-rich stars,<sup>7,8</sup> and the interstellar medium.<sup>9</sup> Given the apparent ubiquity of these species throughout the known universe, there is considerable interest in accurate measurements of their vibrational frequencies and energetics, as these quantities aid in the assignments of astronomical data and in the formulation of chemical mechanisms by which these species are generated and depleted. Here, we report the high-resolution anion photoelectron spectra of cryogenically cooled  $C_7^-$  and  $C_9^-$  linear carbon chains, providing a number of previously unreported vibrational frequencies and insight into the vibronic structure of these important species.

The vast body of experimental and theoretical work concerning carbon clusters has demonstrated clear structural trends in the anionic and neutral  $C_n$  species. Small carbon clusters (n < 10) containing an odd number of atoms have linear geometries while even-numbered clusters have additional energetically low-lying ring structures.<sup>10–12</sup> Larger species  $(n \ge 10)$  preferentially form rings and fullerenes.<sup>13,14</sup> Following this trend, both neutral and anionic  $C_7$  and  $C_9$  are found to be linear cumulenes through experimental and theoretical studies. The neutral clusters have been characterized with ion mobility spectrometry,<sup>15</sup> matrix isolation spectroscopy,<sup>16–23</sup> infrared laser absorption spectroscopy,<sup>24-31</sup> resonant multiphoton ionization spectroscopy,32 and electronic structure calculations.<sup>12,33–35</sup> This body of work shows that both neutral species have closed-shell  ${}^{1}\Sigma_{g}^{+}$  ground electronic states.  ${}^{11,33,36}$ While not as well characterized as their neutral counterparts, the  $C_7^-$  and  $C_9^-$  anions have been found to have openshell  ${}^{2}\Pi_{\varrho}$  and  ${}^{2}\Pi_{u}$  ground states, respectively, from investigations using rare gas matrices,<sup>18,37–39</sup> resonance enhanced multiphoton electron detachment, 40-42 and electronic structure calculations.43-45

Anion photoelectron spectroscopy (PES) is a powerful technique for interrogating the vibronic structure of size-selected neutral clusters via photodetachment of the corresponding anion.<sup>46,47</sup> The first PES study on  $C_7^-$  and  $C_9^-$  was carried out by Yang and co-workers,<sup>48</sup> though these spectra did not have sufficient resolution to extract any vibrational properties of the neutral clusters. Higher resolution PE spectra by Arnold *et al.*<sup>49</sup> yielded vibrationally resolved spectra and electron affinities (EAs) of 3.358(14) and 3.684(10) eV for  $C_7$ 

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and C<sub>9</sub>. Several neutral vibrational frequencies were extracted from these experiments, but these spectra showed a considerable additional unresolved vibrational structure underlying the more intense transitions.

Slow electron velocity-map imaging (VMI) of cryogenically cooled anions (cryo-SEVI) is a high-resolution variant of traditional anion PES wherein cryogenically cooled anions are detached by a tunable laser. The resultant electrons are then detected using a velocity-map imaging (VMI) spectrometer optimized for the detection of slow electrons, giving photoelectron spectra with sub-meV resolution.<sup>50</sup> Previously, we have applied this technique to the  $C_5^-$  carbon chain.<sup>51,52</sup> Here, we report the cryo-SEVI spectra of C7<sup>-</sup> and C9<sup>-</sup>, revealing a considerably more vibrational structure than was seen by Arnold et al.,49 much of which can be assigned by comparison to Franck-Condon (FC) simulations and enabling the measurement of previously unreported vibrational frequencies for C<sub>7</sub> and C<sub>9</sub>. The spectra also show the spin-orbit structure, giving a splitting of 28(6) cm<sup>-1</sup> for the  $C_7^-$  anion, and provide refined EAs of 3.3517(4) and 3.6766(14) eV for C<sub>7</sub> and C<sub>9</sub>. A number of FC-forbidden features are observed for both clusters and are attributed to vibronic coupling effects in either the neutral or anionic species, depending on the symmetry of the neutral excited vibrational state. Finally, an inspection of the photon energy dependence of the cryo-SEVI spectra, complemented by a Dyson orbital analysis, suggests that increasing the length of small linear carbon chains results in the detachment of photoelectrons with higher angular momentum than expected based purely on symmetry considerations.

#### **II. EXPERIMENTAL METHODS**

The cryo-SEVI method has been described in detail previously.<sup>51,53,54</sup> In this work, carbon cluster anions are generated with a laser ablation source using a frequency-doubled Nd:YAG laser focused onto a rotating and translating graphite disk. The resulting plasma is entrained within a pulse of He carrier gas from an Even-Lavie solenoid valve<sup>55</sup> before passing through a skimmer. The ions then pass through a radiofrequency (RF) hexapole ion guide and a RF quadrupole mass filter before being directed into a linear RF octupole ion trap held at 5 K and filled with a buffer gas mixture of 20:80 H<sub>2</sub>:He. Collisions with the cold buffer gas result in effective vibrational, rotational, and electronic cooling of the ions, leading to internal temperatures of around 10 K.<sup>51,56</sup>

After approximately 40 ms, the ions are extracted into an orthogonal Wiley-McLaren time-of-flight mass spectrometer<sup>57</sup> and focused into the interaction region of a VMI electrostatic lens assembly.<sup>58</sup> The cryo-SEVI spectra of  $C_7^-$  and several of the  $C_9^-$  scans were taken using a standard threeplate Eppink-Parker VMI lens assembly, while the remaining  $C_9^-$  data were taken using an updated design utilizing a sevenplate VMI lens.<sup>59</sup> In the VMI spectrometer, ions are photodetached by the frequency-doubled output of a dye laser pumped by the second harmonic of a Nd:YAG laser operating at 20 Hz.

The resulting photoelectrons are projected onto a 2D detector comprising two chevron-stacked microchannel plates

coupled to a phosphor screen, which is photographed by a CCD camera after each laser shot.<sup>60</sup> Each image is analyzed for individual electron events for which the centroids are calculated and binned in a 1024  $\times$  1024 grid.<sup>61</sup> The three-dimensional electron velocity distribution is reconstructed from the accumulated images using the Maximum Entropy Velocity Legendre Reconstruction (MEVELER) algorithm.<sup>62</sup> The radial position of features in the reconstructed image is related to electron kinetic energy (eKE) by acquiring VMI images for detachment from atomic F<sup>-</sup> at several photon energies.<sup>63</sup>

In addition to the eKE distributions, VMI provides the photoelectron angular distribution (PAD) associated with each detachment transition, given by<sup>64</sup>

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{tot}}{4\pi} [1 + \beta P_2(\cos\theta)],\tag{1}$$

where  $\sigma_{tot}$  is the total detachment cross section,  $P_2(x)$  is the second-order Legendre polynomial,  $\theta$  is the angle of the outgoing photoelectron velocity vector with respect to the laser polarization axis, and  $\beta$  is the anisotropy parameter. The anisotropy parameter, which ranges from -1 (perpendicular detachment) to +2 (parallel detachment), reflects the angular momentum of the detached electron and is thus tied to the electronic character of each photodetachment transition.<sup>65</sup>

The VMI spectrometer has an approximately constant resolving power,  $\Delta eKE/eKE$ ,<sup>58</sup> yielding the best eKE resolution for slow electrons. As such, a SEVI spectrum is acquired by first taking an overview spectrum at a relatively high photon energy before tuning the detachment laser to energies slightly above the features of interest. This procedure results in a collection of high-resolution spectra over narrow energy windows that are concatenated and scaled to match intensities in the overview spectrum, which is less sensitive to variation of the photodetachment cross section with photon energy. Spectra are plotted as a function of electron binding energy (eBE), given by eBE = hv - eKE.

#### **III. COMPUTATIONAL METHODS**

Electronic structure calculations for  $C_7^{0/-}$  were carried out at the Spin-Restricted Coupled Cluster Singles Doubles and non-iterative Triples, RCCSD(T)/aug-cc-pVTZ, level of theory<sup>66–68</sup> in order to determine the geometries, normal modes, and harmonic frequencies of the anionic and neutral clusters. Due to the computational expense of performing calculations on  $C_7^{0/-}$  at the RCCSD(T) level, the MP2/ccpVDZ level of theory was chosen to calculate the geometries, normal modes, and harmonic frequencies of  $C_9^{0\bar{\ell}-}$  given its successes in previous studies of carbon clusters<sup>20,69</sup> and similar performance compared to the CCSD(T) level of theory for small clusters.<sup>70</sup> Calculations for  $C_7^{0/-}$  were carried out using the Molpro 2010.1 software package,<sup>71</sup> while those for  $C_9^{0/-}$  were performed using Gaussian 09.<sup>72</sup> Clusters were restricted to linear geometries, as recommended by previous theoretical and experimental studies.<sup>11,36,49</sup> Calculated electron affinities are zero-point corrected, and calculated geometries are presented in Tables S1 and S2 of the supplementary material.



FIG. 1. Cryo-SEVI spectra of the  $\tilde{X}^1 \Sigma_g^+ \leftarrow \tilde{X}^2 \Pi_g$  and  $\tilde{X}^1 \Sigma_g^+ \leftarrow \tilde{X}^2 \Pi_u$  photodetachment of  $C_7^-$  (a) and  $C_9^-$  (b) taken with the ion trap held at 5 K. Low-resolution overview spectra are presented in blue atop high-resolution composite spectra taken at many photon energies. A FC simulation stick spectrum is shown in red.

The equilibrium geometries and normal modes were used to calculate the Franck-Condon profile for the  $\tilde{X}^1 \Sigma_g^+ \leftarrow \tilde{X}^2 \Pi_g$ and  $\tilde{X}^1 \Sigma_g^+ \leftarrow \tilde{X}^2 \Pi_u$  detachment transitions of  $C_7^-$  and  $C_9^-$ , respectively, with the ezSpectrum v3.0 software package.<sup>73</sup> All modes were treated in the harmonic approximation, and FC overlap integrals were calculated using full Duschinsky mixing of all normal modes.<sup>74</sup> To better match the experiment, FC simulations presented in Fig. 1 use scaled vibrational frequencies, as described in Sec. S2 of the supplementary material and presented in Tables S3 and S4. Those using calculated frequencies are presented in Figs. S1 and S2 of the supplementary material, alongside the experimental spectra.

Dyson orbitals for the  $\tilde{X}^1 \Sigma_g^+ \leftarrow \tilde{X}^2 \Pi_g$  and  $\tilde{X}^1 \Sigma_g^+ \leftarrow \tilde{X}^2 \Pi_u$  detachment transitions of  $C_7^-$  and  $C_9^-$ , respectively, were calculated using Q-Chem 4.4 at the EOM-EA-CCSD/6-311++G<sup>\*\*</sup> level.<sup>75–77</sup> These orbitals are one-electron wavefunctions that reflect the change in the electronic structure of the anion upon detachment.<sup>78,79</sup> They were used as an input for the ezDyson v4.0 software package<sup>80</sup> to calculate the total detachment cross section and the partial wave component decomposition of the outgoing electron as a function of eKE (see Table S5 of the supplementary material) by determining the overlap of the Dyson orbital with a plane-wave expansion in a spherical wave basis at the centroid of the Dyson orbital.<sup>81</sup> The resultant anisotropy parameters as well as those extracted from experiment are shown in Figs. S3 and S4 of the supplementary material, and the cross sections are discussed in Sec. V C.

Excited state energies for  $C_7^{0/-}$  and  $C_9^{0/-}$  clusters were calculated utilizing the time-dependent density functional theory (TDDFT) framework at the B3LYP/cc-pVDZ level within Q-Chem 4.4.<sup>75</sup> Calculations were performed using the optimized ground state geometries. To assess the likelihood of vibronic coupling playing a role in the experimental spectra, the derivative coupling vectors<sup>82</sup> (see Sec. S1 of the supplementary material) between the neutral ground states and excited  ${}^{1}\Pi_{u}$  and  ${}^{1}\Sigma_{u}^{+}$  states were calculated for both neutral clusters at the same level of theory. These vectors are illustrated in Figs. S5 and S6 of the supplementary material and discussed in Sec. V B.

## **IV. RESULTS**

The cryo-SEVI spectra of the  $\tilde{X}^1\Sigma_g^+ \leftarrow \tilde{X}^2\Pi_g$  and  $\tilde{X}^1\Sigma_g^+ \leftarrow \tilde{X}^2\Pi_u$  transitions of  $C_7^-$  and  $C_9^-$  are presented in Figs. 1(a) and 1(b), respectively. In both figures, lower resolution overview spectra taken relatively far from threshold (blue) are shown atop higher resolution SEVI scans (black) taken at several photon energies. Simulated FC profiles, scaled to match the intensity of peak A1, are shown as red sticks.

The spectra of both species are dominated by a single peak (A1) attributed to the vibrational origin, above which a considerable vibrational structure is resolved spanning ~3000 cm<sup>-1</sup> in eBE. In the spectrum of  $C_7^-$ , a less intense peak (A1') lies 28 cm<sup>-1</sup> below A1. As our experiment yields vibrationally cold anions,<sup>56</sup> it is unlikely that this structure below the vibrational origin corresponds to a vibrational hot band. We thus assign A1 and A1' to detachment from the lower ( ${}^{2}\Pi_{1/2g}$ ) and upper ( ${}^{2}\Pi_{3/2g}$ ) spin–orbit state of the anion, respectively, to the vibrational ground state of the  ${}^{1}\Sigma_{g}^{+}$  neutral. The minimum peak width achievable for features A1 in the spectrum of  $C_7^-$  and  $C_9^-$ , respectively, is 6 and 22 cm<sup>-1</sup>.

Beyond the vibrational origin, both high-resolution spectra reveal two sets of peaks (A2-A10/B1-B13 in the  $C_7^$ spectrum and A2-A10/B1-B6 in the  $C_9^-$  spectrum) that correspond to transitions to vibrationally excited states of neutral  $C_7$  and  $C_9$ . Positions in eBE and assignments (see Sec. V) of these features are summarized in Tables I and II for the spectra of  $C_7^-$  and  $C_9^-$ , while calculated and experimental parameters obtained for  $C_7$  and  $C_9$ , along with literature values, are summarized in Tables III and IV, respectively. Features are assigned as belonging to the "A" or "B" series of peaks based on several attributes. As discussed below, the "A" and "B" peaks exhibit differing degrees of attenuation at low eKE as well as differing photoelectron angular distributions (in the case of  $C_7^-$ ). Additionally, only the "A" peaks appear in Franck-Condon simulations of the spectra.

TABLE I. Peak positions, shifts from peak A1, and assignments for the SEVI spectra of the  $\tilde{X}^1 \Sigma_g^+ \leftarrow \tilde{X}^2 \Pi_u$  photodetachment of  $C_7^-$  given in Fig. 1(a). All transitions originate from the  $\tilde{X}^2 \Pi_{1/2u}$  state of the anion except those marked with a prime; these transitions originate from the  $\tilde{X}^2 \Pi_{3/2u}$  anion state. Uncertainties in peak positions correspond to one standard deviation obtained from a Gaussian fit to the high-resolution scan of the experimental peak.

Peak	eBE (cm <sup>-1</sup> )	Shift (cm <sup>-1</sup> )	Assignment
A1′	27005(5)	-28	00
A1	27033(3)	0	00
A2	27195(31)	162	$11^{2}_{0}$
B1′	27242(5)	209	$10^{1}_{0}$
B1	27270(3)	237	$10^{1}_{0}$
A3	27346(11)	313	$10^{1}_{0}11^{1}_{0}$
A4	27499(10)	467	$10^2_0$
B2′	27526(4)	493	$10^2_011^1_0$
B2	27553(2)	521	$10^{2}_{0}11^{1}_{0}$
A5	27614(14)	581	$3_0^1$
B3′	27696(4)	663	$10^{3}_{0}$
B3	27722(4)	690	$10^{3}_{0}$
A6	27860(15)	827	$9_0^2$
A7	28004(15)	971	$7_0^2$
A8	28076(11)	1044	$3_0^1 10_0^2$
B4	28131(2)	1098	$3_0^1 10_0^2 11_0^1$
B5	28231(7)	1198	$7^2_0 10^1_0$
B6	28311(5)	1278	$3_0^1 10_0^3$
A9	28602(10)	1570	$2^{1}_{0}$
B7	28931(11)	1899	$5^{1}_{0}$
A10	29152(14)	2119	10
B8	29171(3)	2138	$4_0^1$
B9	29385(4)	2352	$1^{1}_{0}10^{1}_{0}$
B10	29412(4)	2380	$2_0^1 10_0^3 11_0^1$
B11	29647(6)	2614	$2_0^{1}10_0^{4}11_0^{1}$
B12	29664(4)	2631	$2_0^1 3_0^1 10_0^2$
B13	29679(4)	2647	$1_0^1 10_0^2 11_0^1$

TABLE II. Peak Positions, shifts from peak A1, and assignments for the SEVI spectra of the  $\tilde{X}^1 \Sigma_g^+ \leftarrow \tilde{X}^2 \Pi_g$  photodetachment of C<sub>9</sub><sup>-</sup> given in Fig. 1(b). Uncertainties in peak positions correspond to one standard deviation obtained from a Gaussian fit to the high-resolution scan of the experimental peak.

Peak	eBE (cm <sup>-1</sup> )	Shift (cm <sup>-1</sup> )	Assignment
A1	29654(11)	0	00
A2	29844(17)	190	$11_{0}^{2}$
B1	29906(7)	252	$14_{0}^{1}$
A3	30102(12)	448	41
B2	30152(4)	498	130
B3	30344(11)	690	$4_0^1 1 4_0^1$
A4	30560(14)	906	$4_0^2$
B4	30604(4)	950	$4^{1}_{0}13^{1}_{0}$
A5	30924(16)	1270	$3_0^1$
A6	30984(19)	1330	$4_0^3$
A7	31049(23)	1395	$4_0^2 1 4_0^2$
B5	31669(16)	2015	$6^{1}_{0}$
A8	31920(18)	2266	10
A9	31987(22)	2333	$4_0^3 1 3_0^2$
B6	32173(9)	2519	$1_0^{1}14_0^{1}$
A10	32307(14)	2653	$1_0^1 4_0^1$

For both clusters, the distinction between these two groups of features is best depicted in Fig. 2 where the intensity of A1 relative to B1 is shown at several photon energies. Far from threshold (blue curve), A1 is more intense than B1, but as the photon energy decreases, corresponding to detachment of lower-eKE electrons, the cross section of feature A1 is more rapidly attenuated leading to a lower relative intensity. Such differences in the threshold behavior can be related to the relative scaling of the detachment cross sections for low-eKE detachment, which is given by the Wigner threshold law<sup>83</sup>

$$\sigma \propto (\mathrm{eKE})^{l+1/2},\tag{2}$$

TABLE III. Experimental parameters for C<sub>7</sub> extracted from the cryo-SEVI spectrum of the corresponding anion and comparison to the theoretical values obtained in the current work (RCCSD(T)/aug-cc-pVTZ) as well as available literature values. Note that the frequency for  $v_{10}$  is determined from the location of feature B1, as this provides a more precise value than that of A4.

Parameter	RCCSD(T)	Cryo-SEVI	Literature
EA (eV)	3.2677	3.3517(4)	3.358(14) <sup>a</sup>
$v_1(\sigma_g^+)$	2159	2119(14)	
$v_2(\sigma_g^+)$	1554	1570(10)	
$v_3(\sigma_g^+)$	570	581(14)	548(90) <sup>a</sup>
$v_4(\sigma_u^*)$	2198	2138(11)	2138.315 <sup>b</sup>
$v_5(\sigma_u^+)$	1922	1899(5)	1898.376 <sup>c</sup>
$v_6(\sigma_u^+)$	1080		1100.1 <sup>d</sup>
$v_7(\pi_g)$	476	485(10)	496(110) <sup>a</sup>
$v_8(\pi_g)$	138		
$v_9(\pi_u)$	449	414(15)	
$v_{10}(\pi_u)$	240	237(5)	
$v_{11}(\pi_u)$	60	81(22)	

<sup>a</sup>Reference 49.

<sup>b</sup>Reference 24.

<sup>c</sup>Reference 27.

<sup>d</sup>Reference 23.

TABLE IV. Experimental parameters for C<sub>9</sub> extracted from the cryo-SEVI spectrum of the corresponding anion and comparison to the theoretical values obtained in the current work (MP2/cc-pVDZ) as well as available literature values.

Parameter	MP2	Cryo-SEVI	Literature
EA (eV)	4.3029	3.6766(14)	3.684(10) <sup>a</sup>
$v_1(\sigma_g^+)$	2260	2266(21)	
$v_2(\sigma_g^+)$	1901		1871 <sup>b</sup>
$v_3(\sigma_g^+)$	1246	1270(19)	1258(50) <sup>a</sup>
$v_4(\sigma_g^+)$	450	448(17)	484(48) <sup>a</sup>
$v_5(\sigma_u^+)$	2415		2079.67 <sup>c</sup>
$v_6(\sigma_u^+)$	2104	2015(19)	2014.278 <sup>d</sup>
$v_7 (\sigma_u^+)$	1608		1601 <sup>e</sup>
$v_8(\sigma_u^+)$	865		
$v_9(\pi_g)$	579		
$v_{10} (\pi_g)$	320		
$v_{11}(\pi_g)$	131	95(15)	
$v_{12}(\pi_u)$	635		
$v_{13}(\pi_u)$	477	498(17)	
$v_{14} (\pi_u)$	230	252(12)	
$v_{15}(\pi_u)$	51		

<sup>a</sup>Reference 49.

<sup>b</sup>Reference 23.

<sup>c</sup>Reference 29.

<sup>d</sup>Reference 28.

<sup>e</sup>Reference 22.

where  $\sigma$  is the detachment cross section and l is the angular momentum of the detached electron. According to Eq. (2), photodetachment is suppressed more strongly at low eKE for detachment of higher l electrons, owing to the centrifugal barrier experienced by the departing electron. Hence, the "A" peaks appear to correspond to detachment at higher values of

*l* than the "B" peaks. As a consequence, spectra for the "B" peaks can be obtained closer to threshold where cryo-SEVI resolution is better, leading to narrower features. Note that peaks A1 and B1 can be seen at considerably lower eKE values for  $C_7^-$  than for  $C_9^-$ . Since the resolution of cryo-SEVI is highest at low eKE, this difference leads to the larger minimum peak width of A1 in the  $C_9^-$  spectrum, a point considered in more detail in Sec. V C.

The partial wave components that play a role in Eq. (2) are intimately connected to the PADs of different detachment transitions, and differences in threshold behavior often occur concurrently with different PADs.<sup>84</sup> Figure S3 shows that at low eKEs, the PADs of all features in the C<sub>7</sub><sup>-</sup> spectrum are nearly isotropic ( $\beta \approx 0$ ). As the photon energy increases, a discrepancy between the measured values of  $\beta$  for features A1 and B1 begins to form, with feature B1 maintaining  $\beta \approx 0$  and peak A1 showing a more negative anisotropy. This pattern is not apparent in the C<sub>9</sub><sup>-</sup> spectrum; Fig. S4 shows that features A1 and B1 display similar PADs, with roughly isotropic ( $\beta \approx 0$ ) distributions at eKEs ranging from 0.01 to 0.37 eV.

In order to better understand the differing threshold behavior and PADs of these two classes of features, we used the ezDyson software package to calculate total cross sections for the  $\tilde{X}^1\Sigma_g^+ \leftarrow \tilde{X}^2\Pi_g$  and  $\tilde{X}^1\Sigma_g^+ \leftarrow \tilde{X}^2\Pi_u$  transitions of  $C_5^-$ ,  $C_7^-$ , and  $C_9^-$ , shown in Fig. 4. These calculations also provided the expected value of  $\beta$  for these transitions (Figs. S3 and S4 of the supplementary material) and the partial wave component for the detached electron (Table S5 of the supplementary material) as functions of eKE. While all cross sections increase monotonically with eKE, the curvature of the cross section is more complex for  $C_9^-$  than for the other two clusters. The predicted



FIG. 2. Detachment spectra of  $C_7^-$  (a) and  $C_9^-$  (b) at several photon energies illustrating the differing signal attenuation for peak A1 versus peak B1 as eKE decreases. The intensity of each scan has been normalized to the intensity of peak B1. For  $C_7$  (a), photon energies used are 28 967 (blue), 27 675 (red), and 27 302 cm<sup>-1</sup> (black), while for C<sub>9</sub> (b), the energies used are 31 249 (blue), 30 768 (red), and 30 280 cm<sup>-1</sup> (black).



FIG. 3. Dyson orbitals of the  $\tilde{X}^1 \Sigma_g^+ \leftarrow \tilde{X}^2 \Pi_u, \tilde{X}^1 \Sigma_g^+ \leftarrow \tilde{X}^2 \Pi_g$ , and  $\tilde{X}^1 \Sigma_g^+ \leftarrow \tilde{X}^2 \Pi_u$  transitions of C<sub>5</sub><sup>-</sup>, C<sub>7</sub><sup>-</sup>, and C<sub>9</sub><sup>-</sup> calculated at the EOM-EA-CCSD/6-311++G<sup>\*\*</sup> level.

value of  $\beta$  for detachment from C<sub>7</sub><sup>-</sup> as a function of eKE is slightly positive at low eKE (0.01 eV) and decreases dramatically as the eKE increases (0.75 eV), while that of the C<sub>9</sub><sup>-</sup> spectrum is nearly isotropic ( $\beta \approx 0$ ) at low-eKEs and becomes roughly parabolic over a similar energy range.

These quantities are intimately related to the Dyson orbitals, which represent the molecular orbital from which the photoelectron is detached.<sup>79,81</sup> Our calculated Dyson orbitals for detachment from  $C_7^-$  and  $C_9^-$ , presented in Fig. 3, are not localized around a single atom as in the case of photodetachment from closed shell anions to form free radicals,<sup>59,85,86</sup> but encompass the entire carbon chain. Additionally, these calculations reveal that the Dyson orbitals display an increasing number of nodes as the chain is lengthened from 5 to 9 atoms. The implications of these findings will be discussed in more detail in Sec. V C.

#### V. DISCUSSION

#### A. Franck-Condon allowed features

The vibrational assignments of peaks in the  $C_7^-$  and  $C_9^$ cryo-SEVI spectra are provided in Tables I and II, respectively. These assignments were informed by the results of our FC simulations as well as the previously reported photoelectron spectrum by Arnold et al.49 Features A1-A10 in the spectra of  $C_7^-$  and  $C_9^-$  are largely reproduced in the simulated spectra and are thus assigned to Franck-Condon allowed transitions within the  $\tilde{X}^1 \Sigma_g^+ \leftarrow \tilde{X}^2 \Pi_g$  and  $\tilde{X}^1 \Sigma_g^+ \leftarrow \tilde{X}^2 \Pi_u$ photodetachment bands of  $C_7^-$  and  $C_9^-$ , respectively. FC allowed transitions include all  $\Delta v$  transitions in totally symmetric vibrational modes ( $\sigma_g{}^{+}$  for these species) and even  $\Delta v$ transitions in non-totally symmetric modes, with the latter typically being weak for  $\Delta v \neq 0$ . A number of features (B1-B13) in  $C_7^-$  and B1-B6 in  $C_9^-$ ) are not present in the FC simulation and are assigned to FC-forbidden transitions terminating in states with odd quanta of excitation along a  $\pi_{\mu}$  or  $\sigma_{\mu}^{+}$  vibrational mode; these assignments will be justified in Sec. V B. Tables S3 and S4 list the symmetries for all vibrational modes of both species, as well as experimental and theoretical frequencies.

Several features—A1, A5, and A7 in  $C_7^-$ , and A1, A3, and A5 in  $C_9^-$ —were resolved in the lower-resolution spectrum of Arnold *et al.*;<sup>49</sup> these were assigned as the  $0_0^0$ ,  $3_0^1$ , and  $7_0^2$  transitions in  $C_7$  and the  $0_0^0$ ,  $4_0^1$ , and  $3_0^1$  transitions in  $C_9$ . Our improved resolution gives refined values for the EA (3.5117 ± 0.0004 eV) as well as the symmetric stretching and  $\pi_g$  bending frequencies ( $v_3 = 581 \pm 14 \text{ cm}^{-1}$  and  $v_7 = 485 \pm 10 \text{ cm}^{-1}$ ) of neutral  $C_7$ , neglecting anharmonicity in the  $v_7$ mode. Similarly, we are able to extract improved values for the EA (3.6766 ± 0.0014 eV) as well as the symmetric stretching frequencies ( $v_3 = 1270 \pm 19 \text{ cm}^{-1}$  and  $v_4 = 448 \pm 17 \text{ cm}^{-1}$ ) of neutral  $C_9$ .

In the spectrum of  $C_7^-$ , comparison of the cryo-SEVI spectrum to our simulated FC profile allows the assignment of newly resolved stretch fundamentals  $2_0^1$  (A9) and  $1_0^1$  (A10) as well as the doubly excited  $\pi_g$  bends  $11_0^2$  (A2),  $10_0^2$  (A4), and  $9_0^2$  (A6). These give frequencies of 2119(14), 1570(10), 414(15), 234(7), and 81(22) cm<sup>-1</sup> for the previously

unreported  $v_1$ ,  $v_2$ ,  $v_9$ ,  $v_{10}$ , and  $v_{11}$  modes, respectively. A similar analysis in the spectrum of C<sub>9</sub><sup>-</sup> allows for the assignment of the stretch fundamental  $1_0^1$  (A9) and the doubly excited asymmetric bend  $11_0^2$  (A2), giving frequencies of 2266(21) and 95(15) cm<sup>-1</sup>, respectively, for these two previously unreported modes.

As a result of the spin–orbit splitting in the  ${}^{2}\Pi_{g}$  state of the  $C_7^-$  anion, several peaks are split into doublets (A1/A1', B1/B1', B2/B2', B3/B3'). Peaks A1', B1', B2', and B3' each sit 28 cm<sup>-1</sup> below sharp features with similar labels (A1, B1, B2, and B3, respectively), corresponding to the splitting between the  ${}^{2}\Pi_{1/2g}$  and  ${}^{2}\Pi_{3/2g}$  spin-orbit levels of the C<sub>7</sub><sup>-</sup>  ${}^{2}\Pi_{g}$  ground state, in good agreement with values calculated at the RCCSD(T) level of theory.<sup>42</sup> Due to the lower intensity of the peaks originating from the  ${}^{2}\Pi_{3/2g}$  spin–orbit state, compounded with the low intensity relative to A1 for features B4-B13 and A2-A10, only the transitions corresponding to detachment from the lower anion spin-orbit level are observed for these vibrational transitions. Based on the intensity ratio A1'/A1 and the extracted spin-orbit splitting, we obtain a spin-orbit temperature of 14 K for C7<sup>-</sup>, consistent with temperatures previously reported for ions cooled in our ion trap.51,87,88

#### B. Franck-Condon forbidden features

We now consider the vibrational assignments of the "B" series of peaks in both spectra, which are not present in our FC simulations. The spacing in both the B1-A4-B3 progression and between a number of A and B features in the spectrum of  $C_7^-$  (A7  $\rightarrow$  B5, A8  $\rightarrow$  B6, A10  $\rightarrow$  B9) is ~235 cm<sup>-1</sup>, which matches well with our experimentally determined value for  $v_{10}$  of 234(7) cm<sup>-1</sup>. Additionally, the separation between a number of A and B features (B1  $\rightarrow$  A3, A4  $\rightarrow$  B2, A8  $\rightarrow$  B4) is on the order of  $\sim 60 \text{ cm}^{-1}$ , which is congruent with our calculated and experimental values for the  $v_{11}$  mode of 60 and 81(22) cm<sup>-1</sup>. Similarly, in the spectrum of C<sub>9</sub><sup>-</sup>, features B1 and B2 sit 252 and 498 cm<sup>-1</sup> above the vibrational origin, matching well with our unscaled MP2/cc-pVDZ frequencies of the  $v_{14}$ and  $v_{13}$  bending modes at 230 and 477 cm<sup>-1</sup>, respectively. We again see other features with anomalous threshold behavior sitting either ~250 cm<sup>-1</sup> (A3  $\rightarrow$  B3, A8  $\rightarrow$  B6) or ~500 cm<sup>-1</sup>  $(A3 \rightarrow B4)$  above features with poor threshold behavior, suggesting involvement of the  $v_{14}$  and  $v_{13}$  bending modes in these features as well. We thus tentatively assign peaks B1-B6, B9-B13 in the  $C_7^-$  spectrum (B1-B4, B6 in the  $C_9^-$  spectrum) to transitions involving odd quanta along the non-totally symmetric  $v_{10}$  and  $v_{11}$  ( $v_{14}$  and  $v_{13}$ ) vibrational modes, which are of  $\pi_u$  symmetry.

Such transitions are Franck-Condon forbidden, but can arise from Herzberg-Teller (HT) coupling to an excited electronic state with the appropriate symmetry.<sup>89</sup> Consider vibronic states *a* and *b* with electronic and vibrational symmetries  $\Gamma_{elec}$  and  $\Gamma_{vib}$ , respectively. These two states can be HT-coupled provided

$$\Gamma^{a}_{elec} \otimes \Gamma^{a}_{vib} \otimes \Gamma^{b}_{elec} \otimes \Gamma^{b}_{vib} \supset \Gamma_{TS}, \tag{3}$$

where  $\Gamma_{TS}$  is the totally symmetric representation within the molecular point group. If detachment to state *b* is FC-allowed,

i.e.,  $\langle b | \Psi_{anion} \rangle \neq 0$ , detachment to state *a* will reflect the electronic character of state *b*. This will then be reflected in the PADs and threshold behavior of these detachment transitions.

Following Eq. (3), these levels with  $\Gamma_{vib}^a = \pi_u$  and  $\Gamma_{elec}^a = \Sigma_g^+$  can only be observed if they mix with a state *b* that is FC-allowed for detachment from the anion, i.e.,  $\Gamma_{vib}^b = \sigma_g^+$ . Thus, the observed features must arise from HT-coupling to an excited electronic state of  $\Pi_u$  symmetry. In C<sub>7</sub>, such a state has been found experimentally in neon matrices<sup>18</sup> to lie 2.28 eV above the ground electronic state; this has been confirmed by Kolbuszewski who calculated a vertical term energy of 2.64 eV at the Multi-Reference Double-Excitation Configuration Interaction using the Langhoff-Davidson correction, denoted MRD-CI(+Q), level.<sup>33</sup> While the analogous excited state for C<sub>9</sub> has not been seen experimentally, our TDDFT calculations indicate that a  ${}^{1}\Pi_u$  state exists 2.80 eV above the ground state of the neutral.

In the case of  $C_7^-$ , the presence of vibronic coupling is affirmed by the discrepancy observed in the deferring PADs of features A1 and B1 at high eKE,<sup>84,90</sup> as shown in Fig. S3. Peaks A1-A10 display a decrease in the anisotropy parameter  $\beta$  with increasing eKE, consistent with our calculated PAD for the  $\tilde{X}^1 \Sigma_g^+ \leftarrow \tilde{X}^2 \Pi_g$  transition (see Fig. S3 of the supplementary material). Conversely, features B1-B13 show isotropic PADs for all eKEs, which is characteristic of l = 0detachment channels and consistent with these features originating from a state with different electronic character than that giving rise to A1-A10.

The assignment of these features as involving neutral states with excitation along  $v_{10}$  and  $v_{11}$  ( $v_{13}$  and  $v_{14}$  in C<sub>9</sub>) is further supported by the derivative coupling vector<sup>82,91</sup> calculated between the  ${}^{1}\Sigma_{g}^{+}$  ground and the  ${}^{1}\Pi_{u}$  excited state of C<sub>7</sub> and C<sub>9</sub>, which appear as a superposition of the  $v_{10}$  and  $v_{11}$  ( $v_{13}$  and  $v_{14}$  in C<sub>9</sub>) vibrational modes (see Fig. S5 and S6 of the supplementary material). This indicates that the coupling between these electronic states occurs along the  $v_{10}$  and  $v_{11}$  ( $v_{13}$  and  $v_{14}$  in C<sub>9</sub>) normal coordinates, resulting in relatively strong mixing of vibronic states involving excitation along these modes.

Note that three features, B7 and B8 in  $C_7^-$  and B5 in  $C_9^-$ , are assigned to transitions involving odd quanta along the  $\sigma_u^+$ symmetric  $v_5$  and  $v_4$  modes of  $C_7$  and the  $v_6$  mode of  $C_9$ , respectively. These assignments are made based on the agreement between the peak centers (1899, 2138, and 2015  $\text{cm}^{-1}$ ) and the experimentally observed gas-phase frequencies of 2138.315, 1898.376, and 2014.278 cm<sup>-1</sup> for the  $v_5$  and  $v_4$ modes of  $C_7$  and the  $v_6$  mode of  $C_9$ , respectively.<sup>24–28,31</sup> Transitions involving odd quanta along this FC forbidden mode could be explained by invoking HT-coupling in the neutral, which would require an excited neutral state of  $\Sigma_u^+$  symmetry according to Eq. (3). The lowest state of this symmetry has been observed in neon matrices to reside 5.535 and 4.20 eV above the ground state of C<sub>7</sub> and C<sub>9</sub>, respectively.<sup>18</sup> Our calculations at the TD-B3LYP/cc-pVDZ level, however, indicate that the matrix coupling element between the ground electronic and  ${}^{1}\Sigma_{\mu}^{+}$  excited state of both C<sub>7</sub> and C<sub>9</sub> is identically zero, suggesting that these features do not originate from HT-coupling to an excited neutral state.

These nominally FC-forbidden transitions may, however, result from vibronic coupling in the anion. If the vibronic ground state of the anion ( $\Gamma_{vib}^a = \sigma_g^+$ ,  $\Gamma_{elec}^a = \Pi_g$  for C<sub>7</sub><sup>-</sup>, and  $\Gamma_{elec}^a = \Pi_u$  for C<sub>9</sub><sup>-</sup>) couples to another vibronic level *b* which has  $\sigma_{\mu}^{+}$  vibrational symmetry, the *b*-character in the anion ground state would result in nonzero Franck-Condon overlap with the  $\sigma_{\mu}^{+}$ -symmetric neutral vibrational levels for detachment from the vibrationally cold anions. This would require coupling to an excited state with  $\Pi_u$  ( $\Pi_g$ ) symmetry for the  $C_7^-$  ( $C_9^-$ ) anion. Forney and co-workers have observed these states as the lowest-lying excited states for both species, residing 1.978 and 1.622 eV above the ground state<sup>92</sup> of the  $C_7^$ and C<sub>9</sub><sup>-</sup> anions, respectively. This proposition is supported by our TD-B3LYP/cc-pVDZ calculations, as the magnitude of the matrix coupling element between the ground and excited state for both anions is comparable to the coupling element between the neutral ground and  ${}^{1}\Pi_{u}$  excited state invoked above (see Table S6 of the supplementary material).

# C. Angular momentum trends in detachment from linear carbon chains

Based on symmetry arguments alone,<sup>93</sup> s-wave (l = 0)photodetachment near threshold is expected to dominate for detachment from a  $\pi_u$  orbital, the singly occupied molecular orbital in  $C_5^-$  and  $C_9^-$ , whereas in  $C_7^-$ , *p*-wave detachment is the lowest-order partial wave that can occur. From the Wigner threshold law, Eq. (2), one would expect the photodetachment cross section of  $C_5^-$  and  $C_9^-$  to be larger than for  $C_7^-$  near threshold due to the centrifugal barrier inhibiting detachment for larger l. While this expectation is fulfilled for  $C_5^-$ , the results in Fig. 2 indicate that the intensity of the vibrational origin actually drops off more quickly for  $C_9^-$  than for  $C_7^$ as the eKE is lowered. This effect limits the attainable resolution for FC-allowed peaks in C9<sup>-</sup>, as the signals are weak at low eKE where the experimental resolution is the highest. To explore the origin of this effect, consideration of the Dyson orbitals for the three anions and the partial wave contributions to the photodetachment cross section is necessary.

To assess the cross sections associated with the detachment transitions described by the calculated Dyson orbitals, we have utilized the ezDyson software package. Given the symmetry of the Dyson orbitals and the linear  $C_n$  (n = odd) cluster family, the partial-wave expansion performed by ezDyson is localized on the central atom of each molecule and at low eKEs, is dominated by contributions from that atom's local environment. The structure of our Dyson orbitals around this central atom thus impacts these calculations both in the shape of the orbital locally around this central atom and the amplitude of this wavefunction.

From Fig. 3, the Dyson orbitals around the central atom of  $C_5^-$  and  $C_9^-$  appear similar to an atomic *p* orbital, while for  $C_7^-$ , the local orbital looks like an atomic *d* orbital, leading to *s*-wave detachment from the former and *p*-wave detachment from the latter at low eKEs. At higher energies, where effects of the centrifugal barrier are less dominant, the increasing nodal structure of these orbitals for longer carbon chains favors spatial overlap with outgoing partial-waves of higher *l*. As can be seen in Table S5 of the supplementary material, photoelectrons with eKE = 0.10 eV are predominantly detached via the



FIG. 4. Calculated cross sections using ezDyson v4.0. The input to ezDyson was Dyson orbitals for the  $\tilde{X}^1\Sigma_g^+ \leftarrow \tilde{X}^2\Pi_u$ ,  $\tilde{X}^1\Sigma_g^+ \leftarrow \tilde{X}^2\Pi_g$ , and  $\tilde{X}^1\Sigma_g^+ \leftarrow \tilde{X}^2\Pi_u$  detachment transitions of C<sub>5</sub><sup>-</sup>, C<sub>7</sub><sup>-</sup>, and C<sub>9</sub><sup>-</sup>, respectively. All calculations were performed at the EOM-EA-CCSD/6-311++G<sup>\*\*</sup> level. The total cross section is in atomic units.

*s*-wave for both  $C_5^-$  and  $C_9^-$ , while  $C_7^-$  is detached via the *p*-wave. Upon reaching eKE = 0.51 eV, *s*- and *p*-wave detachment is still dominant for  $C_5^-$  and  $C_7^-$ , respectively, while *d*-wave detachment has become dominant from  $C_9^-$ . These findings are commensurate with our PAD measurements for detachment from  $C_5^-$  and  $C_7^-$ .<sup>52</sup> Furthermore, as the three Dyson orbitals presented have similar amplitude, the increased nodal structure results in lower amplitude at the expansion center. This results in lower calculated detachment cross sections near threshold, as seen in Fig. 4, and is in agreement with the observation that the signal near threshold worsens as the chain length is increased.

Collectively, this analysis reveals that while conventional symmetry arguments correctly assess the detachment behavior of this family of clusters very near to threshold (eKE  $\sim 0.10$  eV), they fail to correctly predict behavior at moderate eKEs. Conversely, a Dyson orbital analysis qualitatively predicts the behavior of this class of linear clusters for all observed eKEs and can be understood by treating the local character of the Dyson orbital on the central atom as a quasi-atomic orbital from which the photoelectron is detached. As such, the nodal trend of our calculated Dyson orbitals in which the number of nodes observed increases with the chain length explains the trends we observe in the signal attenuation of this family of clusters near threshold as well as their PADs.

### **VI. CONCLUSIONS**

High-resolution cryo-SEVI spectra of  $C_7^-$  and  $C_9^-$  clusters are reported. We identify the previously unreported  $v_1$  and  $v_2$  symmetric stretches as well as the  $v_9$ ,  $v_{10}$ , and  $v_{11}$  asymmetric bending modes in the neutral  $C_7$  cluster, report a spin–orbit splitting in the  $C_7^-$ , and confirm the assignment of the  $v_3$  and  $v_7$  modes previously reported by Arnold *et al.*<sup>49</sup> In the  $C_9$  cluster, we identify both the  $v_1$  symmetric stretch and asymmetric  $v_{11}$  bend and confirm the previously assigned  $v_3$  and  $v_4$  modes. Coupled cluster and MP2 calculations for  $C_7$  and  $C_9$ , respectively, are used to produce FC-simulated spectra that are able to reproduce one set of our observed features. Those features not explained by FC-simulations are ascribed to the  $v_{10}$  and  $v_{11}$  modes of  $C_7$  and the  $v_{13}$  and  $v_{14}$  modes of  $C_9$ , both

of which appear through Herzberg-Teller coupling between electronic levels of the neutral cluster. Even though s-wave detachment is symmetry-allowed for both  $C_5^-$  and  $C_9^-$ , our experimental results and accompanying calculations indicate that higher partial waves contribute to the photodetachment signal near threshold as the carbon chain length increases.

#### SUPPLEMENTARY MATERIAL

See supplementary material for details regarding the electronic structure, derivative coupling, and Franck-Condon calculations as well as Figs. S1-S6 and Tables S1-S6.

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- <sup>1</sup>W. Weltner and R. J. Vanzee, Chem. Rev. 89, 1713 (1989).
- <sup>2</sup>R. P. A. Bettens and E. Herbst, Astrophys. J. 478, 585 (1997).
- <sup>3</sup>A. Van Orden and R. J. Saykally, Chem. Rev. 98, 2313 (1998).
- <sup>4</sup>E. B. Jochnowitz and J. P. Maier, Annu. Rev. Phys. Chem. 59, 519 (2008).
- <sup>5</sup>A. G. G. M. Tielens, Rev. Mod. Phys. **85**, 1021 (2013).
- <sup>6</sup>A. E. Douglas, Astrophys. J. 114, 466 (1951).
- <sup>7</sup>K. W. Hinkle, J. J. Keady, and P. F. Bernath, Science 241, 1319 (1988).
- <sup>8</sup>P. F. Bernath, K. H. Hinkle, and J. J. Keady, Science 244, 562 (1989).
- <sup>9</sup>E. Herbst, Annu. Rev. Phys. Chem. 46, 27 (1995).
- <sup>10</sup>K. S. Pitzer and E. Clementi, J. Am. Chem. Soc. **81**, 4477 (1959).
- <sup>11</sup>K. Raghavachari and J. S. Binkley, J. Chem. Phys. 87, 2191 (1987).
- <sup>12</sup>J. M. L. Martin and P. R. Taylor, J. Phys. Chem. 100, 6047 (1996).
- <sup>13</sup>R. E. Smalley, Acc. Chem. Res. 25, 98 (1992).
- <sup>14</sup>G. Von Helden, M. T. Hsu, N. Gotts, and M. T. Bowers, J. Phys. Chem. 97, 8182 (1993).
- <sup>15</sup>G. Von Helden, P. R. Kemper, N. G. Gotts, and M. T. Bowers, Science 259, 1300 (1993).
- <sup>16</sup>J. Szczepanski and M. Vala, J. Phys. Chem. **95**, 2792 (1991).
- <sup>17</sup>J. Szczepanski, S. Ekern, C. Chapo, and M. Vala, Chem. Phys. **211**, 359 (1996).
- <sup>18</sup>D. Forney, P. Freivogel, M. Grutter, and J. P. Maier, J. Chem. Phys. **104**, 4954 (1996).
- <sup>19</sup>M. Miki, T. Wakabayashi, T. Momose, and T. Shida, J. Phys. Chem. **100**, 12135 (1996).
- <sup>20</sup>R. H. Kranze, C. M. L. Rittby, and W. R. M. Graham, J. Chem. Phys. 105, 5313 (1996).
- <sup>21</sup>S. Tam, M. Macler, and M. E. Fajardo, J. Chem. Phys. 106, 8955 (1997).
- <sup>22</sup>M. Vala, T. M. Chandrasekhar, J. Szczepanski, and R. Pellow, High Temp. Sci. 27, 19 (1988).
- <sup>23</sup>E. Gonzalez, C. M. L. Rittby, and W. R. M. Graham, J. Phys. Chem. A 115, 2533 (2011).
- <sup>24</sup>J. R. Heath, R. A. Sheeks, A. L. Cooksy, and R. J. Saykally, Science 249, 895 (1990).
- <sup>25</sup>J. R. Heath and R. J. Saykally, J. Chem. Phys. **93**, 8392 (1990).
- <sup>26</sup>J. R. Heath and R. J. Saykally, J. Chem. Phys. **94**, 1724 (1991).
- <sup>27</sup>J. R. Heath, A. Van Orden, E. Kuo, and R. J. Saykally, Chem. Phys. Lett. 182, 17 (1991).
- <sup>28</sup>A. Van Orden, H. J. Hwang, E. W. Kuo, and R. J. Saykally, J. Chem. Phys. 98, 6678 (1993).
- <sup>29</sup>A. Van Orden, R. A. Provencal, F. N. Keutsch, and R. J. Saykally, J. Chem. Phys. **105**, 6111 (1996).
- <sup>30</sup>R. Casaes, R. Provencal, J. Paul, and R. J. Saykally, J. Chem. Phys. **116**, 6640 (2002).
- <sup>31</sup>J. Krieg, V. Lutter, F. X. Hardy, S. Schlemmer, and T. F. Giesen, J. Chem. Phys. **132**, 224306 (2010).
- <sup>32</sup>A. E. Boguslavskiy and J. P. Maier, J. Chem. Phys. **125**, 094308 (2006).

- <sup>33</sup>M. Kolbuszewski, J. Chem. Phys. 102, 3679 (1995).
- <sup>34</sup>P. Botschwina, Theor. Chem. Acc. **104**, 160 (2000).
- <sup>35</sup>Z. X. Cao, S. D. Peyerimhoff, F. Grein, and Q. Zhang, J. Chem. Phys. 115, 2062 (2001).
- <sup>36</sup>J. Kurtz and L. Adamowicz, Astrophys. J. **370**, 784 (1991).
- <sup>37</sup>J. Szczepanski, S. Ekern, and M. Vala, J. Phys. Chem. A **101**, 1841 (1997).
- <sup>38</sup>P. Freivogel, M. Grutter, D. Forney, and J. P. Maier, Chem. Phys. **216**, 401 (1997).
- <sup>39</sup>J. Szczepanski, J. Fuller, S. Ekern, and M. Vala, Spectrochim. Acta Part A. 57, 775 (2001).
- <sup>40</sup>M. Ohara, H. Shiromaru, and Y. Achiba, J. Chem. Phys. **106**, 9992 (1997).
- <sup>41</sup>M. Tulej, D. A. Kirkwood, G. Maccaferri, O. Dopfer, and J. P. Maier, Chem. Phys. **228**, 293 (1998).
- <sup>42</sup>N. M. Lakin, M. Pachkov, M. Tulej, J. P. Maier, G. Chambaud, and P. Rosmus, J. Chem. Phys. **113**, 9586 (2000).
- <sup>43</sup>J. D. Watts and R. J. Bartlett, J. Chem. Phys. **97**, 3445 (1992).
- <sup>44</sup>P. Botschwina, Chem. Phys. Lett. **354**, 148 (2002).
- <sup>45</sup>M. G. Giuffreda, M. S. Deleuze, and J. P. Francois, J. Phys. Chem. A 106, 8569 (2002).
- <sup>46</sup>D. G. Leopold, J. Ho, and W. C. Lineberger, J. Chem. Phys. 86, 1715 (1987).
- <sup>47</sup>A. W. Castleman and K. H. Bowen, J. Phys. Chem. 100, 12911 (1996).
- <sup>48</sup>S. Yang, K. J. Taylor, M. J. Craycraft, J. Conceicao, C. L. Pettiette, O. Cheshnovsky, and R. E. Smalley, Chem. Phys. Lett. **144**, 431 (1988).
- <sup>49</sup>D. W. Arnold, S. E. Bradforth, T. N. Kitsopoulos, and D. M. Neumark, J. Chem. Phys. **95**, 8753 (1991).
- <sup>50</sup>M. L. Weichman and D. M. Neumark, Annu. Rev. Phys. Chem. **69**, 101 (2018).
- <sup>51</sup>C. Hock, J. B. Kim, M. L. Weichman, T. I. Yacovitch, and D. M. Neumark, J. Chem. Phys. **137**, 244201 (2012).
- <sup>52</sup>M. L. Weichman, J. B. Kim, and D. M. Neumark, J. Chem. Phys. 139, 144314 (2013).
- <sup>53</sup>A. Osterwalder, M. J. Nee, J. Zhou, and D. M. Neumark, J. Chem. Phys. 121, 6317 (2004).
- <sup>54</sup>D. M. Neumark, J. Phys. Chem. A **112**, 13287 (2008).
- <sup>55</sup>U. Even, J. Jortner, D. Noy, N. Lavie, and C. Cossart-Magos, J. Chem. Phys. 112, 8068 (2000).
- <sup>56</sup>J. B. Kim, C. Hock, T. I. Yacovitch, and D. M. Neumark, J. Phys. Chem. A 117, 8126 (2013).
- <sup>57</sup>W. C. Wiley and I. H. Mclaren, Rev. Sci. Instrum. **26**, 1150 (1955).
- <sup>58</sup>A. T. J. B. Eppink and D. H. Parker, Rev. Sci. Instrum. 68, 3477 (1997).
- <sup>59</sup>M. L. Weichman, J. A. DeVine, D. S. Levine, J. B. Kim, and D. M. Neumark, Proc. Natl. Acad. Sci. U. S. A. **113**, 1698 (2016).
- <sup>60</sup>D. W. Chandler and P. L. Houston, J. Chem. Phys. 87, 1445 (1987).
- <sup>61</sup>M. B. Doyle, C. Abeyasera, and A. G. Suits, NuACQ, http://faculty.missouri.edu/suitsa/NuAqc.html.
- <sup>62</sup>B. Dick, Phys. Chem. Chem. Phys. 16, 570 (2014).
- <sup>63</sup>C. Blondel, C. Delsart, and F. Goldfarb, J. Phys. B:At., Mol. Opt. Phys. 34, L281 (2001).
- <sup>64</sup>J. Cooper and R. N. Zare, J. Chem. Phys. 48, 942 (1968).
- <sup>65</sup>A. Sanov, Annu. Rev. Phys. Chem. **65**, 341 (2014).
- <sup>66</sup>R. A. Kendall, T. H. Dunning, and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
- <sup>67</sup>P. J. Knowles, C. Hampel, and H. J. Werner, J. Chem. Phys. **99**, 5219 (1993).
- <sup>68</sup>J. D. Watts, J. Gauss, and R. J. Bartlett, J. Chem. Phys. **98**, 8718 (1993).
- <sup>69</sup>J. M. L. Martin, J. P. Francois, and R. Gijbels, J. Chem. Phys. **93**, 8850 (1990).
- <sup>70</sup>J. M. L. Martin, J. Elyazal, and J. P. Francois, Chem. Phys. Lett. **242**, 570 (1995).
- <sup>71</sup>H. J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schutz, Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2, 242 (2012).
- <sup>72</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B.
- Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin,

K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, GAUSSIAN 09, Revision C.01, Gaussian, Inc., Wallingford, CT, 2009.

- <sup>73</sup>V. A. Mozhayskiy and A. I. Krylov, ezSpectrum v3.0, iOpenShell Center for Computational Studies of Electronic Structure and Spectroscopy of Open-Shell and Electronically Excited Species, Los Angeles, http://iopenshell.usc.edu/downloads.
- <sup>74</sup>F. Duschinsky, Acta. Physicochim. U. R. S. S. **7**, 551 (1937).
- <sup>75</sup>A. I. Krylov and P. M. W. Gill, Wiley Interdiscip. Rev.: Comput. Mol. Sci. 3, 317 (2013).
- <sup>76</sup>C. M. Oana and A. I. Krylov, J. Chem. Phys. **127**, 234106 (2007).
- <sup>77</sup>H. Y Shao, Z. T. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. T. Feng, D. Ghosh, M. Goldey, P. R. Horn, L. D. Jacobson, I. Kaliman, R. Z. Khaliullin, T. Kus, A. Landau, J. Liu, E. I. Proynov, Y. M. Rhee, R. M. Richard, M. A. Rohrdanz, R. P. Steele, E. J. Sundstrom, H. L. Woodcock, P. M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G. J. O. Beran, Y. A. Bernard, E. Berquist, K. Brandhorst, K. B. Bravaya, S. T. Brown, D. Casanova, C. M. Chang, Y. Q. Chen, S. H. Chien, K. D. Closser, D. L. Crittenden, M. Diedenhofen, R. A. DiStasio, H. Do, A. D. Dutoi, R. G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, J. Gomes, M. W. D. Hanson-Heine, P. H. P. Harbach, A. W. Hauser, E. G. Hohenstein, Z. C. Holden, T. C. Jagau, H. J. Ji, B. Kaduk, K. Khistyaev, J. Kim, J. Kim, R. A. King, P. Klunzinger, D. Kosenkov, T. Kowalczyk, C. M. Krauter, K. U. Lao, A. D. Laurent, K. V. Lawler, S. V. Levchenko, C. Y. Lin, F. Liu, E. Livshits, R. C. Lochan, A. Luenser, P. Manohar, S. F. Manzer, S. P. Mao, N. Mardirossian, A. V. Marenich, S. A. Maurer, N. J. Mayhall, E. Neuscamman, C. M. Oana, R. Olivares-Amaya, D. P. O'Neill, J. A. Parkhill, T. M. Perrine, R. Peverati, A. Prociuk, D. R. Rehn, E. Rosta, N. J. Russ, S. M. Sharada, S. Sharma, D. W. Small, A. Sodt, T. Stein, D. Stuck, Y. C. Su, A. J. W. Thom, T. Tsuchimochi, V. Vanovschi, L. Vogt, O. Vydrov, T. Wang, M. A. Watson, J. Wenzel, A. White, C. F. Williams, J. Yang, S. Yeganeh, S. R. Yost, Z. Q. You, I. Y. Zhang, X. Zhang, Y. Zhao, B. R. Brooks, G. K. L. Chan, D. M. Chipman, C. J. Cramer, W. A. Goddard, M. S. Gordon, W. J. Hehre, A. Klamt, H. F. Schaefer, M. W. Schmidt, C. D. Sherrill, D. G. Truhlar, A. Warshel, X. Xu, A. Aspuru-Guzik, R. Baer, A. T. Bell, N. A. Besley, J. D. Chai, A. Dreuw, B. D. Dunietz, T. R. Furlani, S. R. Gwaltney, C. P. Hsu, Y. S. Jung, J. Kong, D. S. Lambrecht, W. Z. Liang, C. Ochsenfeld, V. A. Rassolov, L. V. Slipchenko, J. E. Subotnik, T. Van Voorhis, J. M. Herbert, A. I. Krylov, P. M. W. Gill, and M. Head-Gordon, Mol. Phys. 113, 184 (2015).
- <sup>78</sup>O. Dolgounitcheva, V. G. Zakrzewski, and J. V. Ortiz, Int. J. Quantum Chem. 90, 1547 (2002).
- <sup>79</sup>M. Spanner, S. Patchkovskii, C. Y. Zhou, S. Matsika, M. Kotur, and T. C. Weinacht, Phys. Rev. A 86, 053406 (2012).
- <sup>80</sup>S. Gozem and A. I. Krylov, ezDyson v4.0, iOpenShell Center for Computational Studies of Electronic Structure and Spectroscopy of Open-Shell and Electronically Excited Species, Los Angeles, http://iopenshell.usc.edu/downloads.
- <sup>81</sup>C. M. Oana and A. I. Krylov, J. Chem. Phys. **131**, 124114 (2009).
- <sup>82</sup>J. M. Herbert, X. Zhang, A. F. Morrison, and J. Liu, Acc. Chem. Res. 49, 931 (2016).
- <sup>83</sup>E. P. Wigner, Phys. Rev. 73, 1002 (1948).
- <sup>84</sup>J. A. DeVine, A. A. Taka, M. C. Babin, M. L. Weichman, H. P. Hratchian, and D. M. Neumark, J. Chem. Phys. **148**, 222810 (2018).
- <sup>85</sup>J. A. DeVine, M. L. Weichman, M. C. Babin, and D. M. Neumark, J. Chem. Phys. **147**, 013915 (2017).
- <sup>86</sup>M. L. Weichman, J. B. Kim, and D. M. Neumark, J. Phys. Chem. A **119**, 6140 (2015).
- <sup>87</sup>J. A. DeVine, M. L. Weichman, X. Y. Zhou, J. Y. Ma, B. Jiang, H. Guo, and D. M. Neumark, J. Am. Chem. Soc. **138**, 16417 (2016).
- <sup>88</sup>M. L. Weichman, J. B. Kim, and D. M. Neumark, J. Chem. Phys. 140, 104305 (2014).
- <sup>89</sup>G. Herzberg, "Electronic spectra and electronic structure of polyatomic molecules," in *Molecular Spectra and Molecular Structure* (Van Nostrand Reinhold Company, Princeton, NJ, 1966), Vol. 3.
- <sup>90</sup>K. M. Ervin and W. C. Lineberger, J. Phys. Chem. **95**, 1167 (1991).
- <sup>91</sup>Q. Ou, S. Fatehi, E. Alguire, Y. H. Shao, and J. E. Subotnik, J. Chem. Phys. 141, 069903 (2014).
- <sup>92</sup>D. Forney, M. Grutter, P. Freivogel, and J. P. Maier, J. Phys. Chem. A 101, 5292 (1997).
- <sup>93</sup>K. J. Reed, A. H. Zimmerman, H. C. Andersen, and J. I. Brauman, J. Chem. Phys. 64, 1368 (1976).