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Vibronic effects in the photon energy-dependent photoelectron spectra of the CH_3CN^- dipole-bound anion

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Photoelectron spectra are reported for the “dipole-bound” CH_3CN^- negative ion at three photodetachment energies (1.165, 2.331, and 3.496 eV), where the anion is prepared by photodissociation of the $\text{I}^- \cdot \text{CH}_3\text{CN}$ ion–molecule complex. While all three spectra are dominated by a single feature centered near zero electron binding energy, as expected for a dipole-bound anion, vibrational structure is also observed and found to depend strongly on the photodetachment energy. This observation indicates that the vibrational excitation is not exclusively due to distortion between the ion and neutral, but also involves non-“Franck–Condon” effects. The origin of the energy dependence is traced to excitation of the π_{CN}^* shape resonance corresponding to the valence or “chemical” anion. The vibrational envelope of the nonresonant spectrum is surprisingly similar to the infrared spectrum of *neutral* acetonitrile, suggesting that even this excitation may not result from intramolecular distortions. We develop a simple model to illustrate that vibrational excitation can occur upon photodetachment of a dipole-bound electron due to the perturbation of the weakly bound electron by the fluctuating dipole moment of the vibrating neutral molecule. We treat this effect in a Herzberg–Teller interaction picture where the dipole-bound state is mixed with the low lying electron continuum through a dipolar interaction with the neutral molecule. © 1996 American Institute of Physics. [S0021-9606(96)00717-5]

I. INTRODUCTION

One of the more novel aspects of recent work on gas phase ions involves the synthesis and characterization of ground state “dipole-bound” molecular anions. These species are sometimes formed when an electron becomes attached to a closed shell neutral molecule through the long range interaction with the molecular electric dipole moment, provided that moment is above a critical value ($\mu > 2\text{--}2.5$ D).¹ The prototypical example of a dipole-bound system appears to be the negative ion of acetonitrile, CH_3CN^- , which was first observed by Stockdale *et al.*² in 1974. Theoretical work by Jordan *et al.*³ indicated that the ion contains a diffuse electron, and this suggestion was corroborated experimentally by Klahn *et al.*⁴ and Hasemi *et al.*⁵ Most recently, Desfrancois *et al.*⁶ succeeded in field detaching the excess electron with modest external electric fields (< 12 kV/cm), providing the best evidence to date that CH_3CN^- indeed contains a highly delocalized, labile electron.

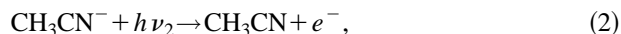
One of the principle reasons that acetonitrile behaves in such a textbook fashion surely arises from the fact that the lowest valence orbital (LUMO) which can accommodate the excess electron, the π_{CN}^* orbital antibonding along the CN bond, is almost 3 eV above the onset of the electron continuum,⁷ so that there is little interaction between the physically bound ground state and the lowest valence state of the negative ion. In the current view, the ground state

CH_3CN^- ion is regarded as an unperturbed neutral molecule tethered to a distant electron which can be easily detached by modest perturbations (fields, collisions, etc.).⁸ Recent high level *ab initio* calculations⁹ support this picture, predicting that the anionic geometry is essentially the same as the neutral geometry with very little excess electron localization on the nominally neutral framework. If the calculations accurately describe the extent of electron delocalization, the photoelectron spectrum of the CH_3CN^- ion should contain only a single sharp feature at the dipole binding energy (~ 18 meV).⁶ It was of interest, therefore, when Bowen and co-workers¹⁰ recorded photoelectron spectra of the related $(\text{CH}_3\text{CN} \cdot \text{H}_2\text{O})^-$ complex (and its deuterated analogs) at 2.540 eV, which revealed significant vibrational excitation of the neutral complex during photodetachment. To clarify the origin of these vibrational features in the hydrate, we report in this paper the results of a photoelectron spectroscopic study of the bare CH_3CN^- anion. As this ion is among the first nominally “dipole-bound” molecular anions to be studied using photoelectron spectroscopy,^{11,12} its qualitative detachment behavior is of interest as it reflects some general aspects of the application of photodetachment and photoelectron spectroscopies to dipole-bound species. We focus on the energy dependence of the detachment cross sections and effects caused by the resonance arising from the covalent molecular anion state where the excess electron occupies the LUMO of neutral CH_3CN .

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II. EXPERIMENT

CH_3CN^- was prepared by photodissociation of the $\text{I}^- \cdot \text{CH}_3\text{CN}$ complex at a fortuitous absorption in the photofragmentation spectrum at 3.496 eV, as described previously.¹¹ Thus Nd:YAG lasers could be used to generate the CH_3CN^- molecule and to obtain its photoelectron spectrum at several different wavelengths through the processes



where $h\nu_1 = 3.496$ eV and $h\nu_2 = 1.165, 2.331$, and 3.496 eV. The experiment was carried out using a pulsed, negative ion mass spectrometer described elsewhere.¹³ The starting $\text{I}^- \cdot \text{CH}_3\text{CN}$ ion-molecule complex was synthesized in an ionized, pulsed free jet expansion containing the ambient vapor pressures of CH_3CN and CH_3I in several atmospheres of argon. Field-detachment studies of CH_3CN^- prepared in this way indicate a stripping onset ≈ 2 kV/cm which gradually increases to complete detachment at the sharp value found when the ion was prepared by Rydberg electron transfer.^{6,8} This difference suggests that the ion produced by photodissociation must possess significant internal excitation. Desfrancois *et al.*⁶ recovered a binding energy of about 18 meV from the onset at higher field, providing a bound on the extent of internal excitation in our experiment. Field detachment experiments have also been carried out at Johns Hopkins using a nozzle ion source¹⁰ to prepare CH_3CN^- which also displayed a detachment onset at ~ 2 kV/cm but leveled off at about 5 kV/cm at 70% detachment. These results indicate that subtle variations in each source give distinct internal energy distributions of CH_3CN^- .

In an earlier paper,¹¹ we presented photoelectron spectra of CH_3CN^- in which photoexcitation and photodetachment were carried out at the same point in the mass spectrometer using different harmonics from the same laser in an arrangement where CH_3CN^- was never actually isolated. While those spectra indicated a very low electron binding energy, the signal to noise was insufficient to resolve vibrational features. In this paper, we have improved the signal to noise in the photoelectron spectra by extensive signal averaging (10^6 laser shots in Fig. 2) to allow analysis of the vibrational fine structure. We have also verified that the carrier of the spectra is indeed the CH_3CN^- anion by photodissociating the $\text{I}^- \cdot \text{CH}_3\text{CN}$ parent cluster in the ion source, mass selecting the CH_3CN^- fragment, and then photodetaching the electron from the fragment ion with a second laser. Using the isolated dipole-bound anion, we were also able to determine the photodetachment cross sections at the photon energies 2.331 and 3.496 eV *relative* to that at 1.165 eV by monitoring the fast photoneutral production at measured laser fluence. Since photodetachment is the only photoprocess at all wavelengths, the fast photoneutral signal is not affected by the energy or angular dependence of the outgoing electron and reflects the total electron detachment yield at each wavelength. The relative cross sections are obtained by measuring the photoneutral intensities at 2.331 and 3.496 eV vs that at 1.165 eV for the same ion beam, and then correcting this raw ratio for the

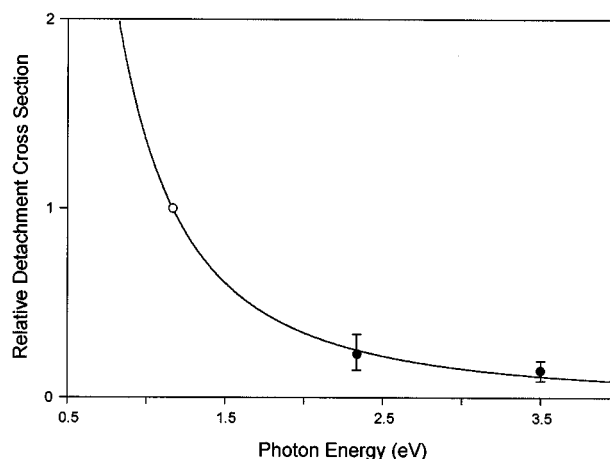


FIG. 1. Relative photodetachment cross section versus photon energy for CH_3CN^- . Points are normalized to the 1.165 eV value, which is included as the open circle at unity. The error in the two relative cross sections contains a contribution from the 1.165 eV measurements. The curve displays a fit to $\sigma \propto (h\nu)^{-2}$.

relative fluence in each laser beam. Due to subtle differences in the beam shapes of the Nd:YAG harmonics, these fluence values are estimated to be accurate to only about 30%.

The time-of-flight photoelectron spectrometer has the capability to decelerate or accelerate photoelectrons uniformly once they are in the drift region to reduce the usual degradation in energy resolution with increasing photon energy. Since photodetachment occurs in a field-free region, the angular distributions of the ejected electrons could also be determined.

III. RESULTS

A. Relative photodissociation cross sections

In an earlier report, where CH_3CN^- was generated and detached with the same laser,¹¹ we remarked that the photodetachment cross sections fell rapidly with increasing photon energy such that even though all three wavelengths (1064, 532, and 355 nm) were present with similar fluence, the sequential two-photon photoelectron spectrum was dominated by 1064 nm detachment. A more quantitative measurement of this effect is presented in Fig. 1, which shows the relative photodetachment cross sections at three photon energies, normalized to the 1.165 eV value. The curve through the points is a fit to $\sigma \propto (h\nu)^{-2}$, indicating that the cross section falls off approximately as the inverse of the square of the photon energy.

The qualitative fall off in the photodetachment cross section observed in Fig. 1 is expected for an anion with a diffuse, weakly bound electron, although this demonstration appears to be the only reported example outside of our earlier work on photodestruction of the $(\text{H}_2\text{O})_n^-$ cluster ions.¹⁴ The CH_3CN^- case does, however, provide a clearer example of the effect. Since the wave function of a dipole-bound excess electron is much larger (≈ 30 Å)¹⁵ than the CH_3CN neutral molecule, dipole-bound anions should be accurately described by the separated wave function, Ψ_A

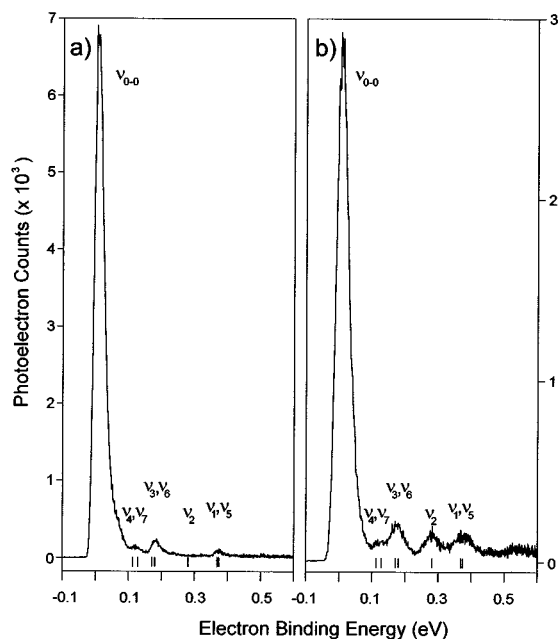


FIG. 2. Photoelectron spectra of CH_3CN^- taken at (a) $h\nu_2 = 1.165$ eV, and (b) $h\nu_2 = 3.496$ eV. See Table I for peak assignments.

$$\Psi_A(r) = \psi_A^{\text{el}} \chi = \psi_D(r) \psi_N \chi, \quad (3)$$

where ψ_A^{el} is the electronic wave function, which can be further separated into the dipole-bound (one electron) wave function $\psi_D(r)$ times the neutral (many electron) wave function, ψ_N , and χ is the vibrational wave function (a product of harmonic oscillators in normal coordinates, Q_i). Photodetachment corresponds to ejection of an electron from the $\psi_D(r)$ orbital, and we generally expect the cross section (which is explicitly derived in Sec. IV) to fall off when this orbital is much larger than the de Broglie wavelength of the ejected electron ($\lambda_D \approx 11.4, 8.1,$ and 6.6 Å for 1.165, 2.331, and 3.496 eV detachment energies, respectively). For the related case of Rydberg electron photoionization, for example, very high energy photoejection cross sections are found¹⁶ to fall off as $\sigma_e \propto (h\nu)^{-3}$. It is not surprising that different exponents are obtained for the Rydberg vs dipole-bound cases, since the Rydberg electron is known to penetrate the core while the dipole-bound electron does not, and the wavelength of the outgoing electron is only a few times smaller than the dimension of the dipole-bound state (~ 30 Å).

B. Photoelectron spectra of CH_3CN^- at 1.165, 2.331, and 3.496 eV

Photoelectron spectra of CH_3CN^- at 1.165 and 3.496 eV photodetachment energies are displayed in Fig. 2. Both spectra are dominated by a single strong feature at nearly zero binding energy [labeled (0–0) with a maximum at 3 meV binding energy], as expected for a dipole-bound anion with a very diffuse excess electron. In the baseline of the main peak, however, lies some reproducible structure in the region corresponding to vibrational excitation, which is distinctly different in the two spectra. (Note that the resolution is no-

ticeably better in the 1.165 eV spectrum, which is normal for a time-of-flight determination of electron kinetic energy). We are primarily interested here in these rather weak features since the nature of the interaction between the excess electron and the neutral should be encoded in the vibrational pattern. The spectra in Fig. 2 were taken with a single laser so that the photofragments were made and detached at the same location in the photoelectron spectrometer. In this configuration, it is possible that the photoelectron spectrum could be contaminated by accidental photodetachment of a long-lived excited state of $\text{I}^- \cdot \text{CH}_3\text{CN}$ based on the dipole moment of CH_3CN .¹¹ While there might not be such a bound state in this system (as the quantum yield for dissociation is quite high), we checked this possibility by also obtaining the photoelectron spectrum from the mass selected CH_3CN^- beam at 1.165 eV, taking advantage of the large cross section and high laser fluence available at this energy. This spectrum is indistinguishable from that in Fig. 2(a), and rules out the possibility that the spectra in Fig. 2 are significantly affected by a putative bound excited state of the parent complex.

The locations of the various vibrational modes of the CH_3CN molecule are displayed in Fig. 2 as vertical lines under the features, indicating that the dominant bands correspond to the C–H stretch (ν_1 and ν_5) and deformation (ν_3 and ν_6) modes of neutral CH_3CN .¹⁷ A smaller band is blended into the main feature near the location of the C–C stretch (ν_4) and CH wag (ν_7) modes. The symmetric (ν_1, ν_3) and antisymmetric (ν_5, ν_6) modes are very closely spaced in CH_3CN and are not resolved in this experiment. The assignment of (ν_1, ν_5) was checked by obtaining the photoelectron spectrum of the CD_3CN^- molecule at 1.165 eV. While the lower frequency modes are compressed into the main band, one feature is distinct and displays the correct isotope shift for the (ν_1, ν_5) assignment. The peak positions in Fig. 2 are compared with the fundamental vibrations of neutral CH_3CN in Table I. Interestingly, the C–N stretch (ν_2) vibration is intense in the 3.496 eV spectrum but *completely absent* in the 1.165 eV spectrum. Note that there is negligible intensity from vibrational hot bands, indicating that either the anion is vibrationally cold or that all vibrationally excited states autodetach prior to photodetachment.

The vibrational region is redisplayed and expanded in Fig. 3, normalized to the intensity of the main (0–0) feature. All of the high frequency features are larger in the higher energy spectrum, with the most striking enhancement involving the ν_2 mode as mentioned above. The smaller peak blended with the main peak (ν_4 and ν_7) displays the least (if any) enhancement. The spectra in Figs. 2 and 3 are taken with the laser polarization oriented along the electron drift axis, which corresponds to the largest photoelectron signal (i.e., asymmetry parameter > 0). With the laser field perpendicular to the flight axis, the vibrations are enhanced relative to the main band (by about 30%) but the spectra are qualitatively similar to those from the more intense parallel polarization. We summarize the relative intensities of the vibrational bands in the parallel configuration at three detachment energies in Table I. Clearly, the ν_2 mode is also intense in the 2.331 eV spectrum, with the intensities of the other vibra-

TABLE I. Vibrational assignments for the photoelectron spectra of CH_3CN^- .

Peak assignment	Literature value (eV) ^a	Experimental value (eV) ^b	Relative peak intensities				
			Calculated ir ^c	PES photodetachment energy ^d			Electron scattering ^e
				1.165 eV	2.331 eV	3.496 eV	
ν_{0-0}		0.003		100	100	100	100
$\nu_4(A_1)$ CC stretch	0.114	0.118	0.44	1.1	0.6	1.9	
$\nu_7(E)$ CH ₃ rock	0.129		0.39				
$\nu_3(A_1)$ CH ₃ sym. deformation	0.172	0.179	0.33	2.7	4.8	5.4	3.7
$\nu_6(E)$ CH ₃ deg. deformation	0.180		2.37				
$\nu_2(A_1)$ CN stretch	0.281	0.283	0.00	0.0	2.6	3.7	3.2
$\nu_1(A_1)$ CH sym. stretch	0.368		0.91				
$\nu_5(E)$ CH deg. stretch	0.373	0.374	0.19	0.7	3.9	4.1	4.4

^aReference 17.^bEstimated error in peak location is ± 5 meV.^cObtained using the intensities from Ref. 9, convoluted with the spectrometer peak shape. Peaks are normalized so that the sum of ν_3 and ν_7 in the simulated spectrum matches the 0.179 eV peak in the 1.165 eV photoelectron spectrum.^dEstimated error in peak intensity is $\pm 10\%$.^eFrom energy loss spectrum taken with 2.9 eV incident electron energy, scattered at 30° . From Fig. 2, Ref. 18.

tional features intermediate between those at 1.165 and 3.496 eV.

C. Summary of results

The main experimental findings of the study are

- the photodetachment cross section of CH_3CN^- falls off rather rapidly in the visible region [$\propto (h\nu)^{-2}$];
- vibrational excitation accompanies photodetachment in such a fashion that the ν_2 mode is strongly enhanced in the visible/uv relative to detachment in the near ir.

The fall off in cross section is expected for a diffuse, dipole-bound system, but the vibrational excitation is not. We discuss possible reasons for the photon-energy dependent vibrational features in the next section.

IV. DISCUSSION

In the usual treatment of photoelectron spectra, vibrational excitation results from a distortion of the anion relative to the neutral. It is therefore somewhat surprising that any

vibrational excitation is observed in the photoelectron spectrum, as recent *ab initio* calculations⁹ predict negligible ($<0.02\%$) intramolecular distortion upon formation of CH_3CN^- . The 3.496 eV spectrum can be reproduced with $\Delta v=1$ Franck–Condon factors arising from distortions of about 1.2% along the totally symmetric (i.e., allowed) CH_3 deformation and CH stretch normal coordinates. This is, however, a rather small distortion consistent with the qualitative picture of the CH_3CN^- ion as a nominally neutral molecule beside a diffuse electron cloud. However, the fact that the spectra are strongly dependent on photon energy rules out the simple interpretation of vibrational excitation due to a geometry change between the ion and neutral.

A. Enhancement of the ν_2 mode in the vicinity of the π^* shape resonance

When a molecular anion adopts the dipole-bound ground state configuration, the state derived from occupation of the excess electron in the valence LUMO of the neutral molecule necessarily lies in the electron scattering continuum (at the equilibrium geometry of the neutral). In this case, the “covalent” form of the ion exists as an electron–molecule scattering resonance. Such resonances can be observed in electron scattering, where the vibrational excitation accompanying formation of the transient negative ion can be used to reveal the nature of the resonance. The lowest energy resonance in $e^-/\text{CH}_3\text{CN}$ scattering lies at about 2.9 eV and corresponds to a π_{CN}^* shape resonance, which is antibonding along the CN coordinate.⁷ Electrons scattered through this resonance cause excitation in several modes of the CH_3CN molecule, but the effect on excitation of the ν_2 (C–N stretching) mode is particularly strong. The energetic situation is summarized in Fig. 4, which depicts the width and location of the resonance relative to the excitation energies available in this experiment. The resonance is monitored by the excitation of $\Delta v=1$ in the ν_2 mode as the electron energy is scanned. The three wavelengths used in the present photodetachment experiments are shown by the horizontal arrows in the figure, and it is clear that both 2.331 and 3.496 eV ex-

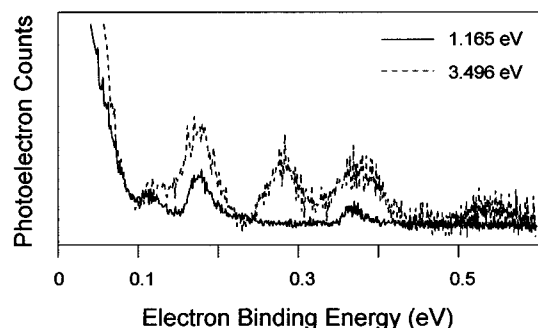


FIG. 3. Expansion of vibrational region of spectra from Fig. 2. The dashed line displays the 3.496 eV spectrum, while the solid line corresponds to the 1.165 eV spectrum. The spectra are normalized to the intensity of the ν_{0-0} feature.

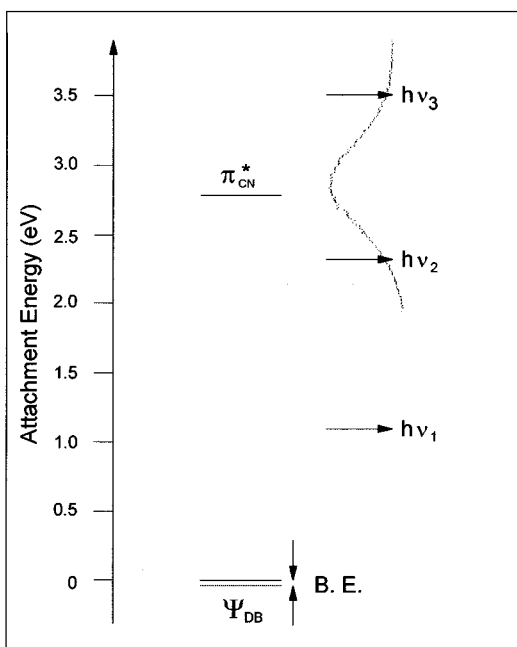


FIG. 4. Diagram of CH_3CN^- energy levels showing the location of the ground state dipole-bound anion and the π_{CN}^* shape resonance centered near 2.9 eV. The horizontal arrows mark the location of the photodetachment energies. The spectrum displayed along the vertical axis indicates the envelope of the π_{CN}^* shape resonance, determined using selective detection of the inelastically scattered electrons by $\Delta v=1$ in the ν_2 mode (reproduced from Ref. 18).

periments fall on the wings of the resonance. The appearance of the ν_2 band in the photoelectron spectra at these energies and not at 1.165 eV, away from the resonance, suggests that photodetachment accesses the transient negative ion state which affects the photoelectron spectrum much like a “half-collision” version of the analogous electron scattering problem.

The C–H stretch and deformation peaks, deriving from modes which are not obviously related to the π_{CN}^* antibonding orbital, are also enhanced in the vicinity of the resonance (Fig. 3). A similar enhancement of these modes is also observed, however, in inelastic electron scattering through the π_{CN}^* resonance, which is explained as a vibronic interaction between the states arising from occupation of the σ^* and π^* orbitals.¹⁸ The relative intensities of the vibrational features in inelastic electron scattering at 2.9 eV are included in Table I (relative to the elastic peak) for comparison with the photoelectron spectra. Clearly, very similar vibrational patterns are observed in the two different experiments. To our knowledge, this is the first such example of photoelectron spectra taken in the neighborhood of a shape resonance, and raises many issues for further study. The important point here is that such phenomena are clearly of general importance in studying photodetachment of dipole-bound anions since the resonance corresponding to the “covalent anion” is often at low energy and easily accessible upon photodetachment in the visible and near uv. For example, the 3.496 and 2.331 eV spectra of CH_3CN^- are remarkably similar to the $(\text{CH}_3\text{CN}\cdot\text{H}_2\text{O})^-$ spectrum (2.54 eV) obtained at Johns

Hopkins¹⁰ in terms of their relative vibrational intensities, and it is now to be determined to what extent the resonance is affecting the spectrum of the hydrated species.

B. 1.165 eV: Vibrational excitation away from the π_{CN}^* resonance

The 1.165 eV photoelectron spectrum [Fig. 2(a)] results from excitation farthest from the π^* resonance, and the ν_2 CN stretch is completely absent from the spectrum. We might now treat this “off-resonant” spectrum as a usual distortion between neutral and anion. As discussed in Sec. III B, if the vibrational envelopes are treated in the Condon approximation, the intensities of the vibrational bands place an upper bound on the intramolecular distortion in CH_3CN of about 1% along the CH stretch and deformation modes, along with a small contribution from ν_4 . Since distortion generally results from partial accommodation of the excess electron in the valence orbitals of CH_3CN , one is led to consider the likelihood of partial charge localization on the molecular framework via the π^* LUMO of CH_3CN . Such charge localization is not supported by recent *ab initio* calculations,⁹ however, which suggest much smaller distortion (<0.02%) than implied by the Franck–Condon fit to the spectrum. We are therefore lead to seek an alternative explanation for the vibrational excitation which does not require a geometry change between the ion and neutral.

When electronic wave functions depend strongly on nuclear coordinates, vibrational excitation can occur without a geometrical distortion due to the $d\psi/dQ$ terms in the coordinate expansion of $\psi_{\text{el}}(r, Q)$ about the equilibrium geometry. In the simplest Herzberg–Teller (HT) treatment of such interactions, the electronic basis wave functions are defined at the equilibrium geometry of the ground state, and are mixed to recover the adiabatic, Q -dependent wave functions. Such vibronic interactions are usually invoked¹⁹ to rationalize the observation of vibrational bands forbidden in the Condon approximation, and we now consider the types of vibronic interactions which are operative in the CH_3CN^- system.

1. Vibronic interactions involving a dipole-bound state

One candidate to mix with the dipole-bound ground state in the case of CH_3CN^- is the localized π^* resonance or covalent anion. However, the matrix elements governing the vibronic interaction should be very small in this case, since the diffuse dipole-bound wave function has little overlap with the orbitals of the localized valence state. One could consider circumventing this restriction by including the indirect interaction between the valence and dipole-bound states through the background, free electron continuum.²⁰ However, as depicted in Fig. 4, the width of the valence (i.e., “ π^* ”) resonance (1 eV) is much less than the energy gap between the dipole and valence states (3 eV), so such a mechanism would be inefficient. This is particularly true since the dipole-bound wave function is itself very similar (in the vicinity of the molecule) to the scattering continuum at low energy, so that the low energy tail of the resonance

directly reflects the lack of interaction between the valence and dipole states. It therefore appears unlikely that a vibronic interaction between the dipole state and the resonance can lead to significant localization by either a direct or an indirect mechanism. We are therefore led to consider another mechanism which can yield a Q dependent, yet “dipolar” wave function.

An intriguing possibility is that the low energy free electron *continuum* can provide the zero order states which mix with the dipole ground state [Eq. (3)] as the nuclei are moved away from equilibrium. The spectral consequences of such a mixing can be explored using the HT scheme to couple the dipole-bound ground state, ψ_A , and the low lying continuum, ψ_c , with each defined at the equilibrium geometry, Q_{eq} , of CH_3CN^- . The details of the treatment are presented in the Appendix, with the main result that

$$\psi_A(r, Q) = \psi_D(r, Q) \psi_N(Q) \chi(Q) \quad (4)$$

with

$$\begin{aligned} \psi_D(r, Q_i) &= \psi_D(r, Q_{\text{eq}}) + F(r) \frac{\partial \mu}{\partial Q_i} Q_i \\ &= \psi_D(r, Q_{\text{eq}}) + \psi_{\text{eff}}^\mu(r), \end{aligned} \quad (5)$$

where $\partial \mu / \partial Q_i$ is the change in dipole moment of the CH_3CN molecule with deformation, Q_i , along one of the normal modes of the molecule. The first order correction arises from $\psi_{\text{eff}}^\mu \equiv F(r) [\partial \mu / \partial Q_i] Q_i$, which is an effective wave function created from a superposition of continuum functions. There are actually two ψ_{eff}^μ functions since normal mode displacements result in a change in dipole moment either parallel or perpendicular to the symmetry axis of the molecule, as discussed in the Appendix. Equation (5) recovers the intuitive expectation that $\psi_D(r, Q)$ is only affected by coordinate displacements which change the dipole moment of CH_3CN and hence the interaction with the excess electron.

The transition dipole moment, \mathbf{M}_{0v} , responsible for vibrational excitation upon photodetachment to level v in the i th mode of the neutral molecule is given by

$$\begin{aligned} \mathbf{M}_{0v} &= \langle \psi_D(r, Q_i) \psi_N(r, Q_i) \chi_0(Q_i) \\ &\quad \times |r| \phi_e(r) \psi_N(r, Q_i) \chi_v(Q_i) \rangle \end{aligned} \quad (6)$$

where $\phi_e(r)$ is the wave function of the photoejected electron and $\chi_0(Q_i)$ is the vibrationless level of the anion. For cases where the dipole-bound wave function of the anion does not depend strongly on Q , this of course reduces to

$$M_{0v}^2 = M_{\text{el}}^2 \langle \chi_0(Q_i) | \chi_v(Q_i) \rangle^2 \quad (7)$$

where $M_{\text{el}}^2 = \langle \psi_D | r | \phi_e \rangle^2$ gives the energy dependence of the detachment cross section (see Sec. III A and Fig. 1) and vibrational excitation is given by the familiar Franck–Condon factor $\langle \chi_0(Q_i) | \chi_v(Q_i) \rangle^2$. For a truly dipole-bound anion displaying little distortion in the molecular core, however, this term is negligible for $v \neq 0$ as the Franck–Condon factors become diagonal. In that case, the explicit coordinate depen-

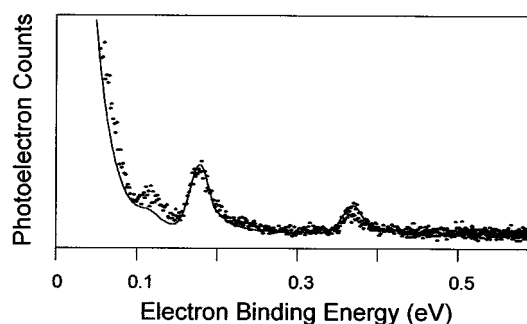


FIG. 5. Overlay of experimental photoelectron spectrum (circles) and neutral CH_3CN ir band intensities (solid line) convoluted to match the resolution of the photoelectron spectrometer.

dence of $\psi_D(r, Q)$ plays an important role in the transition moment. Specializing to the case of parallel vibrational modes, \mathbf{M}_{0v} can be written

$$\begin{aligned} M_{0v} &= \langle \psi_D(r, Q_i) \psi_N \chi_0 | r | \phi_e \psi_N \chi_v \rangle \\ &\equiv \left\langle \left\{ \psi_D(r, Q_{\text{eq}}) + \frac{\partial \mu_{\parallel}}{\partial Q_i} F(r) Q_i \right\} \chi_0 \middle| r \middle| \phi_e \chi_v \right\rangle \\ &\equiv \mathbf{M}_{\text{eff}} \frac{\partial \mu_{\parallel}}{\partial Q_i} \langle \chi_0 | Q_i | \chi_v \rangle, \end{aligned} \quad (8)$$

where \mathbf{M}_{eff} is the Q -independent quantity $\langle F(r) | r | \phi_e(r) \rangle$, which governs the overall intensity of the vibrational envelope. Interestingly, within this envelope, the distribution of intensity among the vibrations is carried by the $d\mu_{\parallel}/dQ_i \langle \chi_0 | Q_i | \chi_v \rangle$ term, which is identical to the operator controlling the intensities of the parallel infrared fundamentals in the neutral molecule! This would appear to be a unique situation, limited to the case of dipole-bound electrons, where coordinate-induced changes in the dipole moment of the neutral molecule have a *direct* effect on the wave function of the excess electron. In this special case, photodetachment from a negative ion should yield a spectrum similar to the infrared spectrum of the corresponding neutral molecule.

Figure 5 presents an expanded view of the vibrations in the 1.165 eV photoelectron spectrum, together with the simulated spectrum expected using the acetonitrile infrared band intensities.⁹ Since we do not know the specific integrals for the parallel and perpendicular modes, we present the spectrum expected from an equal weighting of each type (i.e., the “normal” infrared spectrum). To compare with the photoelectron spectrum, the calculated infrared intensities⁹ were convoluted with line shapes to match the resolution of the photoelectron spectrum. Given the simplistic level of this treatment, there is remarkable similarity between the vibrational envelopes of both spectra. The agreement is particularly good in that it recovers the experimental observation that the peak at 0.179 eV is closer to the degenerate CH_3 deformation (see Table I), which is the strongest in the ir spectrum. Unfortunately, the ν_1 and ν_5 modes are too close together in the 0.377 eV region to cross check this propensity for ir excitation, which should favor the symmetric mode ν_1 .

Although the peak partially blended with the origin is not completely recovered, the overall shape of the observed spectrum is well reproduced by the simulated ir spectrum.

In light of the fact that the ir spectrum is so similar to the off-resonant photoelectron spectrum, we conclude that the vibrational features in the nonresonant photoelectron spectrum of CH_3CN^- need not result from a distortion between the anion and neutral molecular structures, but rather can occur because of the unique aspects of the dipole-bound wave function. In this case vibrational excitation can mimic the infrared absorption spectrum of the “core” neutral molecule.

These considerations raise important issues when photoelectron spectroscopy is used to characterize a dipole-bound anion. While it is common practice in photoelectron spectroscopy to regard vibrational excitation as a consequence of the distortion between the anion and neutral molecule, this usually exceptionally good paradigm may fail when the excess electron's wave function is anomalously strongly dependent on intramolecular distortions associated with large changes in dipole moment (e.g., ir active modes).

V. CONCLUSIONS

We have explored the peculiarities encountered in the application of photoelectron spectroscopy to characterize the CH_3CN^- dipole-bound anion. The very low (~ 3 meV) vertical detachment energy is consistent with a weakly bound, diffuse, dipole-bound electron. The photoelectron spectrum displays an unexpectedly large amount of vibrational structure which can be attributed to two factors. A shape resonance due to the π_{CN}^* orbital at 2.9 eV appears responsible for the photon energy-dependent enhancement of the ν_2 CN stretch, and coupling between π_{CN}^* and σ^* also enhances the CH stretching vibration through the resonance.¹⁸ These resonances should be a general feature of dipole-bound anions since, by definition, the anion state corresponding to occupation of the LUMO at the equilibrium geometry of the neutral lies within the electron continuum. For most systems of chemical interest, the location of such resonances is known through the results of inelastic electron scattering experiments, and can therefore be avoided through a judicious choice of photodetachment energy. Vibrational excitation persists with a different pattern, however, upon nonresonant photodetachment. The intense modes in this spectrum correspond to strong ir bands of neutral CH_3CN . We suggest that these features can arise from the strong coupling of the wave function of the dipole-bound electron to those vibrations in the neutral core that change the dipole moment of the molecule during oscillation. This effect should cause an unusual enhancement of the ir active modes of the neutral molecule in the photoelectron spectrum of the anion. Both the resonant and vibronic effects indicate that vibrational envelopes in the photoelectron spectra of systems with diffuse electrons are probably not due to straightforward Franck–Condon overlaps, and caution is advised when analyzing such spectra.

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APPENDIX: HERZBERG–TELLER TREATMENT OF THE ADIABATIC DIPOLE-BOUND WAVE FUNCTION

In this Appendix, we write out the explicit steps leading to the simple form of Eq. (5), through a Herzberg–Teller interaction between the dipole-bound state and the low lying continuum. We first write the electronic Hamiltonian for CH_3CN^- as

$$H = T_N^e + U_N^e + T_{\text{exs}}^e + U_{\text{exs}}^e(Q_{\text{eq}}) + \Delta U_{\text{exs}}^e(Q) \\ = H_N^0 + H_{\text{exs}}^0(Q_{\text{eq}}) + \Delta U_{\text{exs}}^e(Q), \quad (\text{A1})$$

where T_N^e and U_N^e are the kinetic and potential energy operators for the electrons in neutral CH_3CN , while T_{exs}^e and U_{exs}^e are the same operators for the excess electron. The perturbation term, $\Delta U_{\text{exs}}^e(Q)$, describes the change in the electrostatic interaction between the excess electron and the electrons and nuclei of the CH_3CN molecule upon displacement of the nuclei, Q . This leads to a separable basis for the electronic wave function into the many-electron adiabatic wave function for neutral CH_3CN , $\psi_N(Q)$, and the bound and continuum wave functions describing the excess electron, $\psi_D(r, Q_{\text{eq}})$ and $\phi_E(r, Q_{\text{eq}})$, respectively,

$$\psi_A = \psi_D(r, Q_{\text{eq}}) \psi_N(Q), \quad (\text{A2})$$

$$\psi_c^E = \phi_E(r, Q_{\text{eq}}) \psi_N(Q), \quad (\text{A3})$$

where ψ_A and ψ_c^E are the zero order basis wave functions. We then approximate the adiabatic ground state, ψ_0 , as

$$\psi_0 \approx \psi_A + \int a_E(Q) \psi_c^E dE \\ = \psi_N(Q) \left\{ \psi_D(r, Q_{\text{eq}}) + \int a_E(Q) \phi_E(r, Q_{\text{eq}}) dE \right\}, \quad (\text{A4})$$

where the term in brackets represents the coordinate dependence of the dipole-bound state as a superposition of the continuum states defined at Q_{eq} . The mixing coefficients, a_E , are obtained as usual from the first order perturbation theory matrix elements

$$a_E = \left\langle \psi_N \psi_D \left| \frac{\Delta U_{\text{exs}}(Q)}{E - E_D} \right| \psi_N \phi_E \right\rangle, \quad (\text{A5})$$

where E_D is the energy of the dipole state. Integration of this matrix element over the fast electrons of the CH_3CN molecule yields²¹ an effective operator for the interaction of the excess electron based upon the change in the overall long range dipolar interaction with the molecule

$$\langle \psi_D | \langle \Delta U_{\text{exs}}(Q) \rangle | \phi_E \rangle = \langle \psi_D | \frac{\Delta \mu(Q) \cdot \mathbf{r}}{r^3} | \phi_E \rangle, \quad (\text{A6})$$

where $\langle \Delta U_{\text{exs}}(Q) \rangle$ is the expectation value of the interaction of the excess electron with the CH_3CN molecule at a distance \mathbf{r} relative to the center of mass, and $\Delta\boldsymbol{\mu}$ is the vector describing the change in the expectation value of the dipole moment of the CH_3CN upon displacement of the nuclei, Q , from the equilibrium position, Q_{eq} . In the C_{3v} group, it is useful to resolve the components of $\Delta\boldsymbol{\mu}$ along the directions parallel and perpendicular to the symmetry axis, $d\mu_{\parallel}$ and $d\mu_{\perp}$. We can then write the matrix elements as

$$\begin{aligned} \langle \psi_D | \langle \Delta U_{\text{exs}} \rangle | \phi_E \rangle &\propto \Delta\mu_{\perp} \langle \psi_D | \frac{\sin(\theta)}{r^2} | \phi_E \rangle \\ &+ \Delta\mu_{\parallel} \langle \psi_D | \frac{\cos(\theta)}{r^2} | \phi_E \rangle, \end{aligned} \quad (\text{A7})$$

where θ describes the angle of the excess electron position vector relative to the symmetry (i.e., CCN) axis of the molecule. For the sake of simplicity, we carry the calculation through with only the parallel modes; *both* parallel and perpendicular modes should contribute to $\psi_D(r, Q)$. We can now write the first order correction to the dipole-bound electronic wave function

$$\begin{aligned} \psi_D(r, Q) &= \psi_D(r, Q_{\text{eq}}) \\ &+ d\mu_{\parallel} \int \langle \psi_D | \frac{\cos(\theta)/r^2}{E - E_D} | \phi_E \rangle \phi_E dE, \end{aligned} \quad (\text{A8})$$

The right-hand side of Eq. (A8) has the important property that $d\mu_{\parallel}$ can be taken out of the integral, which can then be replaced by a Q -independent superposition function, $F(r)$

$$\begin{aligned} \psi_D(r, Q) &= \psi_D(r, Q_{\text{eq}}) + d\mu_{\parallel}(Q)F(r) \\ &= \psi_D(r, Q_{\text{eq}}) + F(r) \sum_i \frac{\partial \mu_{\parallel}}{\partial Q_i} Q_i. \end{aligned} \quad (\text{A9})$$

The function $d\mu_{\parallel}F(r)$ is an *effective* wave function which mixes with $\psi_D(Q_{\text{eq}})$ to recover the adiabatic dipolar wave function, $\psi_D(r, Q)$. We note that Eq. (A9) is reminiscent of a Taylor expansion of the wave function where $\partial\psi_D/\partial Q = F(r)[\partial\mu_{\parallel}/\partial Q]$.

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