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Electron binding to valence and multipole states of molecules: Nitrobenzene, para- and meta-dinitrobenzenes

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Nitrobenzene anions (NB^-) in both valence and dipole bound states are examined using laser (photodetachment) photoelectron and Rydberg electron transfer (RET) spectroscopies. Photoelectron spectroscopy of the valence NB^- anion yields a valence (adiabatic) electron affinity of 1.00 ± 0.01 eV. The reaction rates for charge transfer between atoms of cesium and xenon in high Rydberg states [Cs(ns,nd) and Xe(nf)] and NB exhibit a prominent peak in their n-dependencies consistent with the formation of a dipole bound anion having an electron affinity of 28 meV. Para-dinitrobenzene (pDNB) has a zero dipole moment and a large quadrupole moment. RET studies with pDNB show a complex n-dependence. The rate of formation of $pDNB^-$ ions exhibits a broad peak at low n-values and a second very broad feature extending to large n-values. The peak at low n is tentatively attributed to charge exchange into a quadrupole bound state ($EA_{qb}=25$ meV). The absence of field-detachment for these ions suggests that if these are in a quadrupole bound state they are strongly coupled to the valence state. Meta-dinitrobenzene (mDNB) has a large dipole moment and a small quadrupole moment. The observation of a weak but narrow peak at a low n-value in the RET measurement is consistent with electron attachment into a primarily dipole bound state ($EA_{db}=68$ meV) which is also strongly coupled to the valence state. © *1999 American Institute of Physics.* [S0021-9606(99)30534-1]

I. INTRODUCTION

Free electrons are known to attach to molecules via shape, nuclear or electronically excited Feshbach resonances (see review by Schultz[1]). The lifetime of the negative ion intermediate state is a complicated function of the coupling of electronic and nuclear motion. For the case of a pure shape resonance (i.e., no coupling to nuclear motion) the lifetime is very short ($\sim10^{-15}$ s). The lifetime, τ, of a nuclear excited Feshbach resonance is related to the electron capture cross section, σ, through the principle of microscopic reversibility,[2]

$$\tau=(1/v\sigma)(\rho^-/\rho^0), \tag{1}$$

where ρ^- represents the density of states for the negative ion, ρ^0 is the density of states of the free electron plus molecule, and v is the velocity of the incident electron. Many complex molecules are known to form long-lived (1–1000 μs) negative ion states through the sharing of the incident electron energy and electron affinity energy among the many degrees of freedom of the molecule.[3] Unimolecular electron attachment results in anions which are metastable (unless radiation occurs) and the lifetime of the state decreases with increasing total energy in the anion. The quasiequilibrium theory embodied in Eq. (1) has been shown to adequately describe the lifetimes and cross sections for a number of molecules, most notably for the SF_6 molecule.[2] In recent years, this vibrational autodetachment process has been observed in neutral molecules and clusters and has become known as ‘‘thermionic emission’’ (see the review by Klots and Compton[4]).

Fermi[5] was the first to point out that the reaction between an atom in a high Rydberg state and a molecule can be approximated by that of the interaction of a slow quasifree electron with the scatterer together with the polarization induced upon the scatterer by the Rydberg ion core. This model has been successfully applied to electron attachment reactions.[6] In those reactions, the ion core also acts to stabilize the negative ion through removing vibrational energy.

It is often useful to represent the interaction of an electron with an atom or molecule in terms of its static and dynamic electrostatic energies. If we consider only the dipole and quadrupole terms, the potential of interaction between an electron and a molecule is conveniently expressed as

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$$V(r) = -\frac{e\mu}{r^2}P_1(\mathbf{r}\cdot\mathbf{R}) - \frac{eQ}{r^3}P_2(\mathbf{r}\cdot\mathbf{R}) - \frac{\alpha e^2}{2r^4} + L(L+1)\frac{\hbar^2}{2mr^2}, \tag{2}$$

where μ is the electric dipole moment and Q is the quadrupole moment. $P_1(\mathbf{r}\cdot\mathbf{R})$ and $P_2(\mathbf{r}\cdot\mathbf{R})$ are the Legendre polynomials, and the last two terms represent the polarizability attraction and centrifugal repulsion for an electron with angular momentum L with respect to the center of the charge distribution. α represents the polarizability of the atom or molecule.

In recent years, there has been growing interest in the bound states of the electron–atom or electron–molecule system that result from their multipole moments as embodied in Eq. (2). Since only atoms in degenerate states can have a dipole moment (e.g., H), the quadrupole is generally the first nonzero electric moment for atoms. For molecules, the study of the binding of electrons to molecules possessing a dipole moment has a rich history. Fermi and Teller[7] were the first to predict that a fixed (nonrotating) dipole should bind an electron or positron provided that the dipole moment exceeds 1.625 D. By considering the dipole potential outside of a molecule, Crawford and Garrett[8] were able to neglect other effects of the molecular electrons and to show that molecules whose dipole moments are above ~2 D should permanently bind an extra electron (for an interesting historical account of this development see Turner[9]). Rydberg atom charge transfer to polar molecules is one method of preparing the fragile dipole bond anions. Recently, Desfrançois *et al.*[10] have provided direct evidence for dipole bound anions in a series of experiments showing a narrow *n* (principal quantum number) dependence in the Rydberg electron transfer (RET) rate with molecules having dipole moments above the critical moment (now thought to be ~2.5 D). They also used the electric field detachment method introduced by Haberland to show that these anions were weakly bound and to measure electron affinities for many of the polar molecules. The measured affinities fit well with the dipole model. The Villetaneuse group[11] has provided a comprehensive review of ground-state dipole bound anions.

The possibility of electron binding to molecules possessing large quadrupole moments has been under investigation since 1979. The existence of quadrupole bound states of anions was first considered by Jordan[12] who predicted a large electron affinity for $(\mathrm{BeO})_2$ mostly due to the quadrupole attraction. Prasad, Wallis, and Herman[13] further performed calculations which demonstrated a dependence on the sign of the quadrupole moment (i.e., charge distribution) for the binding of an electron to a fixed linear electric quadrupole.[14] As a result of the shorter range for the quadrupole potential, it was not possible for them to make a statement as to the ''critical'' quadrupole moment necessary to bind an extra electron as has been done in the case of the dipole field. In fact, since the quadrupole field falls off as $1/r^3$ the singularity at $r=0$ assures binding (negative energy) for an unrealistic point quadrupole of any magnitude Q. In real molecules at these close distances the details of the atomic and/or molecular structure contribution must be included. In addition, the quadrupole moment is expected to play a role in the binding of electrons to molecules which possess a permanent dipole moment. In some molecules for which the dipole moment is almost large enough to produce a ''dipole bound'' state, the quadrupole moment (along with polarizability) can tip the balance and provide the necessary binding.

Experimental evidence for binding to a molecular quadrupole is scarce and contradictory. However, the interesting negative ion properties of $\mathrm{CS_2}$ has stimulated interest in it as a possible candidate for quadrupole binding. Harth, Ruf, and Hotop[15] were the first to report a very interesting *n* dependence for the $\mathrm{CS_2^-}$ production cross section in collisions with Ne(ns) and Ne(nd) high Rydberg atoms. The cross section exhibited a steep rise at low *n*, a characteristic maximum for $n\sim 18$ and a steep decrease toward higher *n*. A number of years ago, Dunning *et al.*,[16] Carman *et al.*,[17] and Desfrançois' *et al.*,[18] reported a similar *n*-dependence in the Rydberg charge transfer cross section to the $\mathrm{CS_2}$ molecule which is reminiscent of the features exhibited by dipole bound states. Also, Dunning *et al.*[16] further showed that the $\mathrm{CS_2^-}$ anion was easily undergoing field induced electron detachment in the presence of a weak electric field, again characteristic of a weakly bound state. Prompted by these reports, Compton, Dunning, and Nordlander[19] performed calculations which suggested that electron binding to the quadrupole field of $\mathrm{CS_2}(Q=+3.3\,\mathrm{a.u.})$ might account for these results. The absence of weakly bound states and no pronounced peak in the *n* dependence for the formation of COS added further credence to this proposal $[Q(\mathrm{COS})=-0.2\,\mathrm{a.u.}]$. However, given the results of Prasad *et al.*,[13] a negative quadrupole moment of $\mathrm{CO_2}(Q=-3.1\,\mathrm{a.u.})$ should have also led to the formation of a quadrupole bound anion, but no anions were reported for $\mathrm{CO_2}$ in Ref. 16 or 17. It should be pointed out, however, that these anions were not specifically under investigation there and could have eluded detection as a result of their extreme fragility or narrow *n* dependence. Also on the negative side, Gutsev, Bartlett, and Compton[20] have recently reported calculations for the binding energies for $\mathrm{CO_2^-}$, $\mathrm{COS^-}$, and $\mathrm{CS_2^-}$, that were not definite as to the formation of quadrupole bound states.

These experiments can be better understood in light of recent studies which have provided experimental evidence for quadrupole bound states.[21] These diffuse states have been observed and characterized by means of Rydberg electron transfer and field detachment for molecules (e.g., succinonitrile) and clusters (e.g., formamide dimer) which possess null dipole moments but considerably larger quadrupole moments than those considered above. To our knowledge, the only rigorous quantum chemistry calculations dealing with quadrupole bound anions are those of Refs. 12 and 22, but a simple electrostatic model[21] allows consideration of the stability of anions possessing excess electrons which are weakly bound in very diffuse orbitals by multipolar potentials. The existence of a potential well responsible for electron binding is due to the sum of attractive potential terms describing dipolar, quadrupolar, and polarization forces, and a short-range repulsive potential due to the Pauli exclusion of the excess electron from the closed-shell valence orbitals. It can be shown[21] that a single empirical parameter can be employed to describe the repulsive part of the interaction potential. This repulsion parameter is a function of the polarizability with a typical value close to 1. Although this model is rather simple, the accuracy of its prediction is comparable to that of more elaborate ab initio calculations. Typically, the relative error for the prediction of electron binding energies is less than 50%.

In this paper, we report measurements (Rydberg charge exchange and/or photodetachment) on molecules which form long-lived valence anions and which possess either a sufficiently large dipole moment $[\mu(\mathrm{NB})=4.22\,\mathrm{D},\ \mu(\mathrm{mDNB})=4.29\,\mathrm{D}]$ or quadrupole moment $[Q(\mathrm{pDNB})=-59\,\mathrm{a.u.}]$ which might be expected to bind an electron into a diffuse anion state.

II. EXPERIMENT

The experimental methods used here are the same as those employed in our recent study of electron binding to nitromethane.[23] Briefly, charge exchange reactions between excited Rydberg atoms and beams of nitrobenzene were studied at both the University of Paris-Nord using $\mathrm{Xe}(nf)$ Rydberg atoms[10] and at the Oak Ridge National Laboratory using $\mathrm{Cs}(ns,nd)$ Rydberg atoms.[17] In addition, Rydberg charge transfer to meta- and para-dinitrobenzene was studied at the University Paris-Nord. Laser photodetachment negative ion photoelectron spectroscopy of the nitrobenzene negative ion was performed at Johns Hopkins University.

The Rydberg electron transfer method (RET) uses electrons which are initially bound to Rydberg atoms and transferred under single collision conditions to molecular assemblies. In the experiments described herein, laser-excited $\mathrm{Cs}(ns,nd)$ (Ref. 17) or $\mathrm{Xe}(nf)$ (Ref. 11) atoms are allowed to cross beams of molecules or neutral clusters. Ions created by charge transfer are extracted from the collision region and further mass-analyzed in a time-of-flight mass spectrometer. The Rydberg atom principal quantum numbers vary from 7 to 50 (corresponding to mean Rydberg electron energies between 280 and 5 meV). The n-dependencies of the rate constants for the formation of NB^- and p,mDNB^- anions are determined by comparison with SF_6^- signals which are produced by Rydberg atom collisions with thermal effusive beams of SF_6. At high principal quantum numbers n, the Rydberg charge transfer should proceed via attachment into a long-lived nuclear excited Feshbach resonance in accordance with Eq. (1). The attachment into dipole or quadrupole anion states is expected to occur over a narrow range of lower principle quantum numbers n, where resonance charge transfer can occur.

In the photodetachment experiments, NB^- anions were formed by coexpanding nitrobenzene vapor at two different temperatures with several atm argon gas through a 25 μm nozzle. The primary electrons were supplied by a negatively biased ThO/Ir filament placed just outside the nozzle (in the presence of an axial magnetic field) to create a microplasma discharge in the dense region of the expansion. The secondary, thermalized electrons, coming primarily from the argon atoms, attach themselves to the molecules of interest under the influence of cooling collisions. In the past, a wide variety of ground-state dipole bound anions have been generated and photodetached with this source.[24] In cases where the valence anion state is lowest in energy, however, the nozzle ion source preferentially produces the valence anions, as has been demonstrated for nitromethane[23] and for solvated uracil anions.[25] Once the ions are formed, they are then accelerated and transported via a system of ion optical elements through an $\mathbf{E}\times\mathbf{B}$ Wien mass filter, and the resulting mass-selected ion beam is crossed at right angles with the fixed-frequency argon ion laser operated intracavity. Photodetachment spectra were recorded at the wavelengths of 457.9 nm, 488.0 nm, and 514.5 nm. A small solid angle of photoejected electrons was then collected and passed through a hemispherical electron kinetic energy analyzer having a typical resolution of 27 meV. The electron binding energy (EBE), the incident photon energy $(h\nu)$, and the kinetic energy of the photodetached electron (EKE) are related through the conservation of energy, $\mathrm{EBE}=h\nu-\mathrm{EKE}$. This apparatus has been described previously in detail.[26]

III. RESULTS AND DISCUSSION

A. Rydberg charge exchange

Rydberg electron transfer (RET) is a well established method for the production and study of weakly bound anions in which excess electrons occupy very diffuse orbitals.[6,11] In contrast with the source described immediately above, the single collision operating conditions of the RET anion source are such that even very weakly bound anions can survive after electron attachment. The experimental lower limit for the excess electron energy under study is not determined by collisional processes but rather by the accelerating, focusing and/or stray electric fields which can induce field detachment. With careful control of these fields along the anion path, anions with excess electron binding energies as low as 0.3 meV can be produced.[11] The RET signature for the production of such weakly bound anions is the presence of a narrow peak at n_{max} in the RET n-dependence. This Rydberg selectivity in anion production can be understood within the framework of a multiple ionic-covalent crossing model.[27] An empirical law[11] which has been tested with a large number of dipole bound anions (and a few quadrupole bound anions) directly relates the corresponding electron affinity EA to the experimentally determined n_{max} value, $\mathrm{EA(eV)}=23/(n_{\mathrm{max}})^{2.8}$. The signature for creation of valence anions, on the other hand, is the observation of a smooth variation of the RET n-dependencies over a wide range of high n-values. Another method for probing electron binding energies is field detachment by means of an externally applied uniform electric field. Unfortunately, neither RET nor field detachment experiments provide any means of determining valence electron affinities, and one must then rely on PES measurements. Moreover, as was shown in our previous studies of nitromethane,[23] a diffuse state can be more or less strongly coupled to a valence state. The existence of a diffuse state then only appears through the shape of the RET curve which is dominated by the electron transfer at large electron–molecule distances (electron attachment over a wide range of

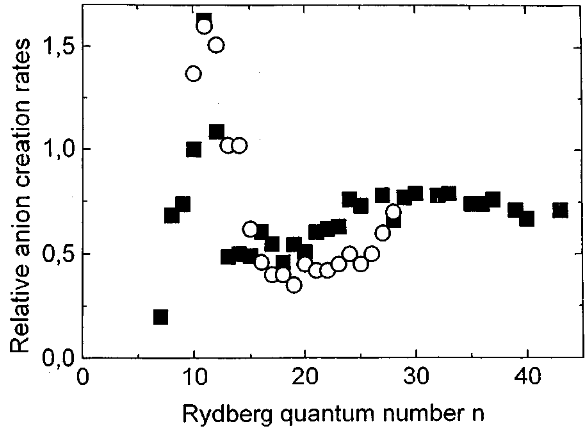

FIG. 1. The *n*-dependence of the relative rate constant for the formation of nitrobenzene anions in collisions of Xe**(nf) (squares) and Cs**(ns,nd) (circles) laser excited atoms with nitrobenzene.

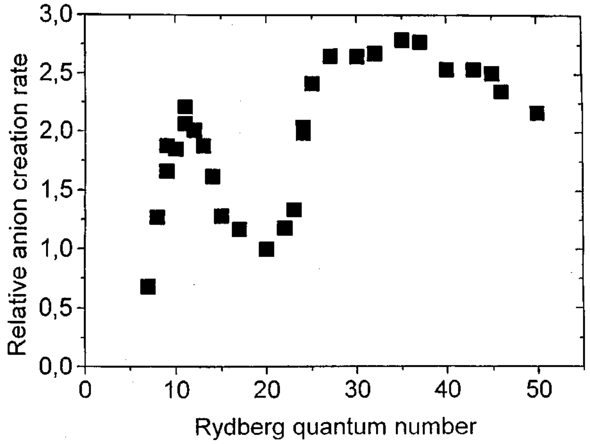

FIG. 2. The *n*-dependence of the relative rate constant for the formation of 1,4-dinitrobenzene anions (pDNB$^-$) in collisions of pDNB with Xe**(nf) atoms.

high *n*-values). The RET *n*-dependence curve is still peaked in this case, but it is broader than for a pure dipole bound or quadrupole bound state. Also, field detachment in the case of coupled states is no longer possible since a fraction of the excess electron orbital is localized at a very short distance near the molecule.

Figure 1 shows the *n*-dependence of the reaction rates for charge transfer between atoms of cesium and xenon in high Rydberg states [Cs(ns,nd) and Xe(nf)] and nitrobenzene (NB). The nitrobenzene oven was kept at 23 °C. The RET *n*-dependence curve exhibits a prominent peak at an effective principal quantum number $n_{\max}=11$. This result is consistent with the formation of a dipole bound anion and the corresponding electron affinity deduced from the empirical formula given above is $\mathrm{EA}_{\mathrm{db}}=28$ meV. There has been one previous report on the effects of the dipole states in the electron/nitrobenzene interaction. Frey *et al.*[28] detected a manifestation of anionic states supported by the dipole field of the nitrobenzene molecule in an inelastic electron–dipole molecule scattering experiment at sub-meV energies.

In order to test the nature of the orbital occupied by the excess electron of the NB$^-$ anions, we have performed field detachment measurements while tuning the laser for production of Xe($11f$) or Xe($25f$) Rydberg atoms. In both cases, no detachment of the NB$^-$ anions was observed. We conclude from the absence of field-detachment of the dipole bound anions (for $n=11$) that there is a strong coupling of the diffuse state to the valence state. Nitrobenzene has a large dipole moment of 4.22 D and a rather small quadrupole moment component along the dipole axis of only -9 a.u. Its parallel and perpendicular polarizabilities are respectively estimated to be 17.3 A^3 and 11.6 A^3. From these values and using the electrostatic model, we calculate an approximate value of the dipole bound electron affinity equal to 30 $\pm$ 10 meV.

The study of RET electron attachment to pDNB was prompted by the anticipation of the observation of quadrupole bound anions. pDNB appears to be a good candidate since its dipole moment is null, and the components of its quadrupole moments are equal to $Q_{zz}=+45$ a.u.; $Q_{yy}=-59$ a.u.; $Q_{zz}=+14$ a.u. The parallel and perpendicular polarizabilities are evaluated to be 22.0 A^3 and 16.6 A^3, respectively. From the simple electrostatic model, we can predict the approximate value of the quadrupole bound electron affinity to be 23 ± 15 meV. The RET *n*-dependence for the production of para-dinitrobenzene ions pDNB$^-$ shown in Fig. 2 displays a peak around $n=11-12$ suggesting the existence of a weakly bound anion. The corresponding experimental electron affinity deduced from the above empirical relationship is about 25 meV. The increase of the anion creation rate between $n=20$ and $n=25$ is similar to that observed for several other anions created by Rydberg electron attachment to aromatic systems. It may be due to Rydberg electron transfer into π orbitals, but until now, no quantitative explanation has been given for this observation. No field-detachment is observed for pDNB$^-$ anions produced by RET from Xe($12f$) atoms. This result and the rather large width of the RET *n*-dependence indicate that the diffuse state is strongly coupled to a valence state. Indeed, it is known[29] that NO$_2$-containing disubstituted benzene derivatives strongly attach epithermal electrons and form long-lived valence negative ions.

The oven containing pDNB was kept at 90 °C, which is a temperature well below the melting point of pDNB (173 °C) but equal to the melting point of mDNB (90 °C). We were thus concerned about the possibility of isomerization taking place in the heated oven, leading to the formation of 1,3-dinitrobenzene (mDNB) from pDNB. In that case, the observed weakly bound anions could be attributed to dipole bound mDNB$^-$ anions. However, the RET method not only provides a nonperturbative ionization process, but also an analytical tool which allows one to distinguish between isomeric pDNB$^-$ and mDNB$^-$ anions. mDNB has a large dipole moment ($\mu=4.29$ D), very close to that of nitrobenzene, and a quadrupole moment of $Q=+18$ a.u. Its parallel and perpendicular polarizabilities are respectively estimated to be 21.2 A^3 and 17 A^3. From the electrostatic model, the predicted electron affinity of mDNB is 105 ± 25 meV, corresponding to a peak in the RET curve around $n=7$. To test for

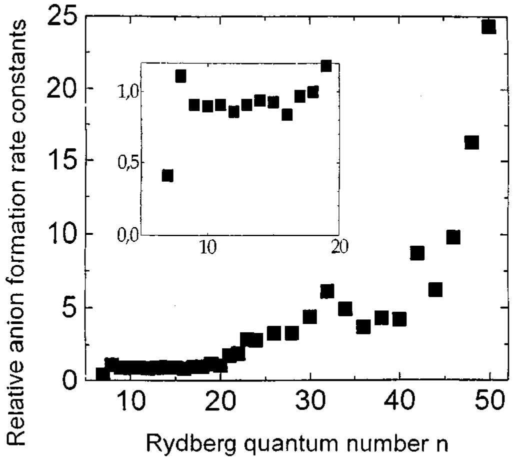

FIG. 3. The n-dependence of the relative rate constant for the formation of 1,3-dinitrobenzene anions (mDNB^-) in collisions of mDNB with $\mathrm{Xe}^{**}(nf)$ atoms. The inset displays the weak peak at $n=8$ corresponding to the dipole bound state of the mDNB^- anion.

isomerization and contamination, we have replaced pDNB with mDNB and studied Rydberg electron transfer to this molecule. The experimental RET n-dependence for the production of meta-dinitrobenzene ions mDNB^- is shown in Fig. 3. This curve is very different from the RET curve corresponding to pDNB. The broad peak at $n=11-12$ has disappeared and is replaced by a very small peak at $n=8$, close to the predicted value for the dipole-bound mDNB^- anion. The anions reported here are not observed to undergo field detachment. This observation is attributed to the coupling of these diffuse states with the ground valence anion state. In our previous study of RET on nitromethane (CH_3NO_2),[23] both the dipole bound and the valence state were observed in direct analogy to the case of nitrobenzene studied here. However, for nitromethane, field detachment of the dipole state was observed for some values of n. We conclude that for the nitrobenzenes reported here, the weakly bound anion states are coupled to the valence anion state more strongly than in the case of nitromethane, probably due to the larger valence electron affinities and number of degrees of freedom in nitrobenzenes.

At the present time, we can only suggest that the pDNB anions formed under Rydberg charge transfer for $n=10-15$ are a result of transfer into a quadrupole bound state. In this connection, a recent theoretical study by Gutowski and Skurski[22] finds that pDNB does not support a quadrupole bound anion state but only a valence anion state. The quadrupole moment tensor reported by that group is however close to the one reported herein. A further possibility therefore is that a short-lived quadrupole state is formed followed by rapid intramolecular conversion to the bound valence state. In this sense, the quadrupole state is a doorway state to the formation of bound valence anions. This issue will only be resolved through further experimental and theoretical studies.

B. Photoelectron (photodetachment) spectra

The photoelectron (photodetachment) studies were undertaken to further explore the energy states of the nitrobenzene anion and their relationship to neutral nitrobenzene. Extensive efforts were devoted to attempts to produce a dipole bound anion of nitrobenzene, since its dipole moment of 4.22 D is considerably larger than the critical value of ~2.5 D necessary to support a stable dipole bound state. In the photodetachment experiments, however, we did not observe the dipole bound anion of nitrobenzene. This was probably due to the tendency of the ion nozzle source to produce only the most stable (in this case, the valence) anion state of a molecule. As a result, the primary contribution of the photodetachment experiment to this study is the characterization of the valence anion state of nitrobenzene.

The photoelectron spectrum of the nitrobenzene anion, recorded at 514.5 nm, is shown in Fig. 4. Notably, there is no photodetachment signal characteristic of a dipole-bound anion. Based on our previous experience[24,25] we would expect the signal due to a transition from a dipole bound anion state to be located near zero electron binding energy and to be distinguished by a single, narrow feature reflecting the nearly identical geometries of the anion and the neutral. The spectrum of NB^-, however, is typical of a valence anion.

The vibrational structure in Fig. 4 is indicative of a substantial difference in the equilibrium geometries of the anion and its neutral. The energy interval between the prominent vibrational peaks is $1345\pm 70\,\mathrm{cm}^{-1}$ and corresponds to the symmetrical $-NO_2$ stretching frequency (literature values[30] are 1345 cm^{-1} in IR or 1351 cm^{-1} in Raman spectra). This result confirms our expectations that the excess electron should be localized on the $-NO_2$ moiety of the molecule. Furthermore, according to the experiments in the gas-phase,[31] in solution,[32] and in the crystal,[33] both the neutral[31] nitrobenzene and its radical anion[32,33] have planar geometry due to the conjugation of the p-orbitals of oxygen atoms with the π-electron orbital of the aromatic ring. Be-

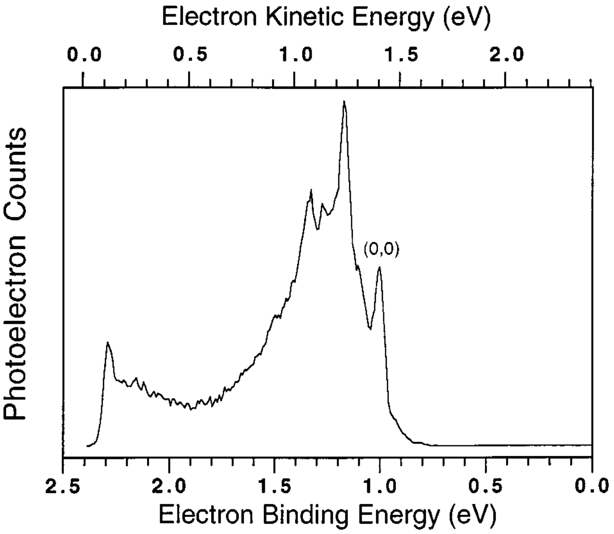

FIG. 4. The photoelectron spectrum of the nitrobenzene valence anion recorded with 514.5 nm (2.409 eV) photons. The origin is indicated as (0, 0).

cause of this restriction in the degrees of freedom for $-\mathrm{NO}_2$ moiety, the primary effect of the excess electron is to lengthen the N–O bonds in the anion. Correspondingly, upon the photodetachment of this electron, primarily the $-\mathrm{NO}_2$ stretch would be excited. This situation is somewhat different from that of a nitromethane anion,[23] where the $-\mathrm{NO}_2$ attached to a methyl group assumed a pyramidal configuration around nitrogen atom upon the attachment of the excess electron. As a result, the most highly populated vibrations in the neutral nitromethane upon photodetachment of the excess electron were $-\mathrm{NO}_2$ bend and $-\mathrm{NO}_2$ wag.

One of the most important physical properties of a molecule deduced from its negative ion photoelectron spectra is its electron affinity, i.e., the measure of the stability of the ion with respect to the neutral. The adiabatic electron affinity (EA_a) is the energy difference between the $v''=0$ level of the ground electronic state of the anion and the $v'=0$ level of the ground electronic state of the neutral. Therefore, in a photoelectron spectrum, EA_a corresponds to the energy of the $v'=0 \leftarrow v''=0$, i.e., the (0, 0) transition. In the absence of ''hot'' bands originating from the vibrationally excited levels of the anion, the (0, 0) transition is the first peak in the vibrational progression [unless the geometrical distortion between the anion and the neutral is so great that the (0, 0) transition is inaccessible through vertical (optical) excitation]. Under the supersonic expansion conditions of this source, the temperature of these anions was probably low, on the order of 10–100 K. However, to explore the possibility of observing hot bands, we recorded spectra at two different temperatures of nitrobenzene vapor, 23 °C and 100 °C. The two spectra taken at these temperatures with 514.5 nm photons are presented in Fig. 5(a). The effect of the higher temperature is seen as only a slight broadening of features. Hot bands are thus probably not an important issue in this spectrum. Consequently, we assign the lowest-EBE resolved vibrational peak as the (0, 0) transition. From the energy of the (0, 0) peak top we determine the EA_a of nitrobenzene to be 1.00 ± 0.01 eV. This value of EA_a agrees well with the previous determinations of 1.01 eV and 0.959 eV by Kebarle and co-workers[34] based on the measurements utilizing gas-phase electron-transfer equilibria. Earlier charge exchange studies reported the lower limit to the adiabatic electron affinity of nitrobenzene to be $>0.7 \pm 0.2$ eV.[35] Estimates were also provided via microscopic reversibility calculations[36] which found EA_a to be ~0.5 eV.

The photoelectron spectra of the nitrobenzene anion were also recorded with 488.0 nm (2.540 eV) and 457.9 nm (2.708 eV) photons, again at two temperatures [Figs. 5(b) and 5(c)]. Note that the relative intensities of individual vibrational peaks in these spectra are wavelength-dependent. Nevertheless, there are wavelength-invariant traits present in all of these spectra. The value of EA_a as determined from any of these spectra is the same, namely 1.00 ± 0.01 eV. Also, the vibrational spacings between the major peaks remain the same, indicating identical modes of vibrational excitation. The additional peak that emerges in the 457.9 nm spectrum is spaced from the neighboring peak by the $-\mathrm{NO}_2$ stretching frequency, just as are the others. Essentially, the peak locations do not change with wavelength. Heating the source from 23 °C to 100 °C has a relatively minor effect on all of these spectra, slightly broadening them but leaving the overall shape unchanged.

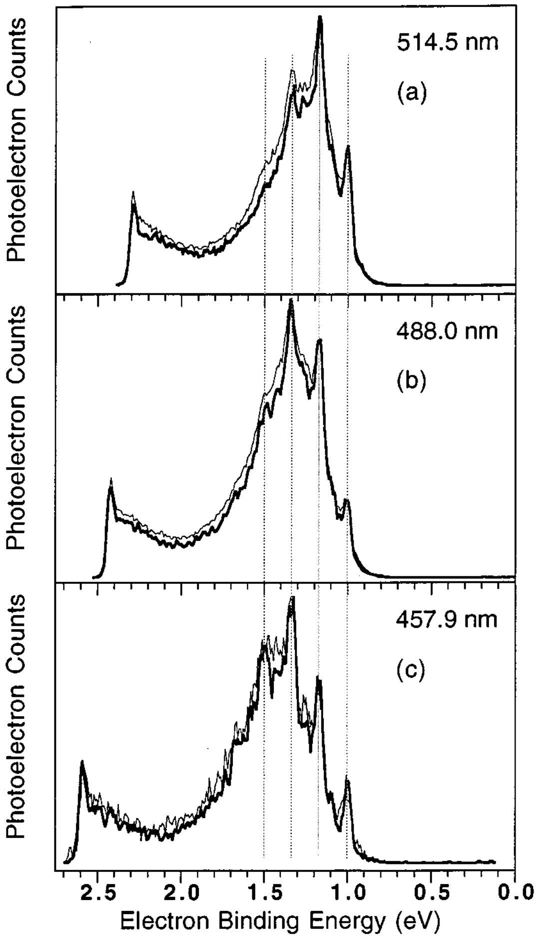

FIG. 5. The photoelectron spectra of the nitrobenzene valence anion recorded with (a) 514.5 nm (2.409 eV), (b) 488.0 nm (2.540 eV), and (c) 457.9 nm (2.708 eV) photons. The thick line spectra were taken at 23 °C, while the hairline spectra were taken at 100 °C.

The observed non-Franck–Condon behavior is probably due to the presence of an excited anion state within the energy range of our photons. Indeed, it has been shown[37] that nitrobenzene molecule captures slow (0–5 eV) electrons. It has three temporary anion resonant states, one of which lies 1.36 eV above the neutral molecule and has a full-width-at-half-maximum of 0.5 eV (the other two states are at 0.55 eV and 4.7 eV). Thus, if one adds the EA_a of NB to 1.36 eV, the above mentioned resonance lies ~2.36 eV above the anion ground state. This temporary anion state is therefore readily accessible from the anion ground state with our photons (from 2.4 to 2.7 eV). As a result, the shape of the photoelectron spectrum of NB^- is influenced by the exact location and the width of this resonance as well as by the photon energy used to reach that state. The degree of the spectral distortion depends on the lifetime of the excited state during which the anion geometry relaxes and departs from the equilibrium ground-state geometry.

In addition, this resonance has been shown to decay both by low kinetic energy electron emission and by dissociation

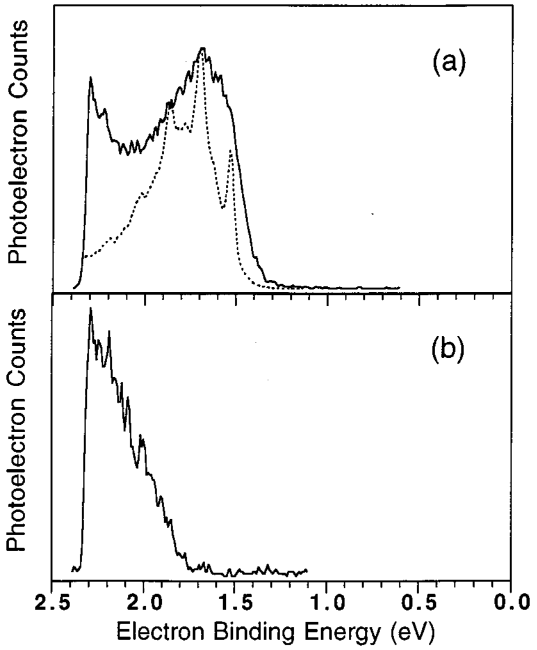

FIG. 6. The photoelectron spectra of (a) NB_2^- and (b) NB_3^- recorded with 514.5 nm photons. The dashed line in (a) shows the spectrum of NB^- shifted by 0.53 eV and superimposed on the spectrum of NB_2^- to demonstrate the similarity of their spectral width.

yielding NO_2^- ions.[3] We observed both an accumulation of near zero kinetic energy electrons in the photoelectron spectra as well as NO_2^- anions in our mass spectrum. Slow electrons and NO_2^- ions are both observed because the dissociation reaction and thermal electron autodetachment proceed via a common temporary negative ion state.[3]

Finally, in addition to the nitrobenzene molecular anion we have also observed nitrobenzene cluster anions NB_n^- and we have recorded the photoelectron spectra of the dimer and the trimer anions (Fig. 6). Two effects are evident; the dimer and trimer anion spectra have lost the resolved vibrational structure of NB^-, and they both have been successively shifted to higher EBE's. Having determined the EA_a for NB^- and NB_2^-, one can evaluate the energy of interaction between a nitrobenzene anion and a neutral nitrobenzene molecule, i.e., the dissociation energy of the dimer anion into NB^- and NB, $D_0(NB^-\cdots NB)$. The following equation relates $D_0(NB^-\cdots NB)$ to the dissociation energy of the neutral dimer $D_0(NB\cdots NB)$ and to the electron affinities, $EA_a(NB)$ and $EA_a(NB_2)$, of the monomer and dimer, respectively,

$$D_0(NB^-\cdots NB)=EA_a(NB_2)-EA_a(NB)+D_0(NB\cdots NB). \tag{3}$$

Upon comparing the width of the photoelectron spectrum of NB^- with that of NB_2^- [see Fig. 3(a)] and seeing that they are similar, we assume that the difference $EA_a(NB_2)-EA_a(NB)$ is roughly equal to the shift of the photoelectron spectrum of the dimer anion relative to that of the monomer anion. This shift is ~0.53 eV. The interaction energy of two neutral nitrobenzene molecules is ~0.14 eV as estimated from extrapolating the experimental plot[38] of the Gibbs free energy of nitrobenzene dimerization (and using electric permittivity $\epsilon=1$ for vacuum). Using Eq. (3), the dissociation energy of the nitrobenzene dimer anion into NB^- and NB is therefore determined to be ~0.67 eV. The EA_a's for NB_2 and NB_3 as estimated from the threshold energies of their anion photoelectron spectra are ~1.5 eV and ~1.8 eV, respectively. The substantial increase in the excess electron binding energy of ~0.5 eV in going from NB^- to NB_2^- may be partially due to the resonance stabilization of the charge in the dimer anion. The trimer anion, on the other hand, lacking the symmetry of the dimer, shows a much smaller increase of only ~0.3 eV relative to NB_2^-.

IV. CONCLUSION

Nitrobenzene, *p*- and *m*-dinitrobenzene anions all have both diffuse and valence states. For nitrobenzene and *m*-dinitrobenzene, the diffuse states may correspond to dipole bound anions. A simple electrostatic model assuming the same geometries of the neutral and its anion enables us to predict dipole bound electron affinities with fair accuracy. Photoelectron spectroscopy reveals large structural differences between neutral NB and its valence NB^- anion. Good agreement between the predicted and the experimentally-determined values of the diffuse-state electron affinities of NB, mDNB, and pDNB leads us to suggest that $pDNB^-$ anions have a quadrupole bound state. The absence of field-detachment for ions initially formed in the diffuse states may indicate that the dipole and quadrupole bound states act as a ''doorway'' to the formation of the more stable valence anion states.

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