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Ab initio electronic structure of HCN^- and HNC^- dipole-bound anions and a description of electron loss upon tautomerization

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The binding of an excess electron to HCN and HNC was studied at the coupled cluster level of theory with single, double, and noniterative triple excitations and with extended basis sets to accommodate the loosely bound excess electron. The HCN molecule, with a dipole moment of 3.05 Debye, binds an electron by 10 cm^{-1}, whereas the HNC tautomer possesses a similar dipole moment (3.08 Debye) and binds the electron by 43 cm^{-1}. The electronic stability of the anionic system along the minimum energy HCN→HNC tautomerization path has been investigated, and it was concluded that the excess electron autodetaches during the tautomerization. Unusually large electron correlation energy contributions to the total electron binding energy were found and are discussed.

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I. INTRODUCTION

A. Anions of hydrogen cyanide and isocyanide

Hydrogen cyanide HCN and hydrogen isocyanide HNC are basic chemical compounds of great importance for inorganic and organic chemistry. They were detected in interstellar clouds and a number of comets, including the Hale–Bopp comet.[1,2] Extensive *ab initio* calculations have been performed to determine the ground-state potential-energy surface of these species; in particular, the HCN→HNC tautomerization process was studied in detail (e.g., see Refs. 3–5 and references therein). However, the number of studies on corresponding anionic species (i.e., HCN^- and HNC^-) is rather limited.

The radical anion of HCN has been observed both in the solid and gas phases. Adrian *et al.*[6a] observed the ESR spectrum of HCN^- produced by ultraviolet (UV) irradiation of cyanide doped alkali halide crystals and obtained the infrared spectrum of this anion, while Tsuda and co-workers[6b] detected HCN^- in the gas phase using mass spectrometry.

There have also been several theoretical attempts undertaken to estimate the electron affinity (EA) of hydrogen cyanide.[7–9] Pacansky *et al.*,[7] on the basis of Hartree–Fock (HF) calculations, obtained a negative value of the adiabatic electron affinity (-1.95 and -2.09 eV, depending on the basis set used) for HCN and, therefore, concluded that its anion should not be stable in the gas phase since it was unlikely, in their opinion, that correlation effects would be sufficiently large to change the sign of the calculated EA. A similar conclusion was made later by Lohr[8] on the basis of HF calculations with 6-31+G** basis sets. Moreover, even though correlation effects were included at the configuration-interaction with single and double excitations (CISD) level, the calculated value of the EA remained negative (with the 6-31+G** basis set).[8] These conclusions have been criticized by Garrett who pointed out that HCN should form a stable dipole-bound anion since its dipole moment of ~3 D exceeds the critical value of 1.625 D needed to bind an excess electron (for point or fixed-finite dipole).[9,10]

To the best of our knowledge, the most early accurate estimate of the EA for HCN, has been given by Jordan and Wendoloski[11] who estimated that the EA (at the Koopmans' theorem level[12]) as 0.0008 eV (6 cm^{-1}). However, since their calculations were performed in rather limited basis sets (6-31 G supplemented with a small set of *s*- and *p*-symmetry diffuse functions), the authors speculated that employing larger basis sets would lead to reducing the dipole moment of HCN (overestimated in their basis set with comparison to the experimental value) which should cause the final electron affinity to be even smaller (~3 cm^{-1}).[11]

In the present work, we provide significantly more accurate calculations of the HCN^- electron binding energy as well as the electron binding energy of the HNC^- anion that has not yet been studied. Moreover, we discuss the electronic stability of the anionic system along the minimum energy HCN→HNC tautomerization path, and with respect to the

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H···CN$^-$ van der Waals complex. Our preliminary results were presented in Ref. 13.

B. Dipole-bound anions

The binding of electrons to polar molecules has been addressed in many theoretical[13–29] studies. It has been shown that, within the Born–Oppenheimer (BO) approximation, a dipole moment greater than 1.625 Debye possesses an infinite number of bound anionic states,[16] although a more practical critical value to experimentally observe a dipole-bound anion was found to be ~2.5 Debye.[17,18]

Jordan and Luken demonstrated that the loosely bound electron in a dipole-bound state occupies a diffuse orbital localized mainly on the positive side of the dipole.[19] This finding was confirmed by many subsequent studies. The role of non-BO coupling has been studied by Garrett, who concluded that such couplings are negligible for dipole-bound states with electron binding energies (D) much larger than the molecular rotational constants.[20]

The simplest theoretical approach to estimate D is based on Koopmans' theorem (KT).[12] The KT binding energy ($D^{\rm KT}$) is the negative of the energy of the relevant unfilled orbital obtained from a Hartree–Fock self-consistent field (SCF) calculation on the *neutral* molecule. Orbital relaxation effects, which are neglected in the KT approximation, have been found to be quite small for a variety of dipole-bound anionic states.[13] In contrast, the role of electron correlation has proven to be very significant. In fact, in many cases the electron binding energy of the dipole-bound anion has been dominated by the contribution from electron correlation.[13,24]

In the present contribution, we examine the dipole-bound anions that result from attaching an electron to the HCN and HNC molecules. Moreover, we investigate the electronic stability of the anionic system along the minimum energy HCN→HNC tautomerization path. We employ extended basis sets and a variety of treatments of electron correlation.

II. METHODS

We studied the ground-state potential-energy surface of the neutral system at the QCISD (quadratic configuration interaction including single and double substitutions)[30] level of theory. We also performed CCSD (coupled-cluster method with single and double excitations) geometry optimizations to check that the geometrical parameters (bond lengths) differ by less than 0.000 01 Å from those found at the QCISD level.

Because the methods we used are based on an unrestricted Hartree–Fock starting point, it is important to make sure that little if any artificial spin contamination enters into the final wave functions. We computed the expectation value $\langle S^2\rangle$ for the HCN$^-$ and HNC$^-$ species and found values of 0.7500 in all cases. Hence, we are certain that spin contamination is not large enough to significantly alter our findings.

The electron binding energies (D) were calculated at the QCISD-optimized geometries of the neutral species since the electron binding in these cases is sufficiently weak that the geometry relaxation upon electron attachment is negligible. We calculated the values of D by using a supermolecular approach (i.e., by subtracting the energies of the anion from those of the neutral). This approach requires the use of size-extensive methods for which we have employed Møller–Plesset perturbation theory up to the fourth order and the coupled-cluster method with single, double, and noniterative triple excitations [CCSD(T)].[31,32] In addition, for both the HCN$^-$ and HNC$^-$ minimum energy structures, D was analyzed within the perturbation framework designed for dipole-bound anions and solvated electrons.[23]

The polarization of the neutral (N) by the excess electron and the effect of back polarization are taken into account when the SCF calculation is performed for the anion (A), and the accompanying induction effects are given by

$$\Delta D_{\rm ind}^{\rm SCF} = D^{\rm SCF} - D^{\rm KT}, \tag{1}$$

where

$$D^{\rm SCF} = E_N^{\rm SCF} - E_A^{\rm SCF}, \tag{2}$$

and $E_N^{\rm SCF}$ and $E_A^{\rm SCF}$ stand for the SCF energies of the neutral and the anion, respectively.

The dispersion interaction between the loosely bound electron and N was extracted from the second-order Møller–Plesset (MP2) contribution to D. The dispersion term is a second-order correction with respect to the fluctuation-interaction operator and it is approximated here by $\Delta D_{\rm disp}^{\rm MP2}$, which takes into account proper permutational symmetry for all electrons in the anion

$$\begin{aligned}\epsilon_{\rm disp}^{(02)} &= \Sigma_{a\in N}\Sigma_{r<s}|\langle \phi_a\phi_{lbe}||\phi_r\phi_s\rangle|^2/(e_a+e_{lbe}-e_r-e_s)\\ &= -\Delta D_{\rm disp}^{\rm MP2},\end{aligned} \tag{3}$$

where ϕ_a and ϕ_{lbe} are *spin–orbitals* occupied in the unrestricted Hartree–Fock (UHF) wave function, ϕ_r and ϕ_s are unoccupied orbitals, and e's are the corresponding orbital energies. The subscript lbe denotes the loosely bound electron's spin orbital.

The total MP2 contribution to D defined as

$$\Delta D^{\rm MP2} = D^{\rm MP2} - D^{\rm SCF} \tag{4}$$

is naturally split into dispersion and nondispersion terms

$$\Delta D^{\rm MP2} = \Delta D_{\rm disp}^{\rm MP2} + \Delta D_{\text{no-disp}}^{\rm MP2}, \tag{5}$$

with the latter dominated by the correlation correction to the static Coulomb interaction between the loosely bound electron and the charge distribution of N.

The higher-order MP contributions to D are defined as

$$\Delta D^{{\rm MP}n} = D^{{\rm MP}n} - D^{{\rm MP}(n-1)}, \quad n=3,4. \tag{6}$$

Finally, the contributions beyond the fourth-order are estimated by subtracting MP4 results from those obtained at the coupled-cluster level

$$\Delta D^{\rm CCSD(T)} = D^{\rm CCSD(T)} - D^{\rm MP4}. \tag{7}$$

The diffuse character of the orbital describing the loosely bound electron (see Fig. 1) necessitates the use of extra diffuse basis functions having very low exponents.[13] In addition, the basis set chosen to describe the neutral molecular host should be flexible enough to (i) accurately describe

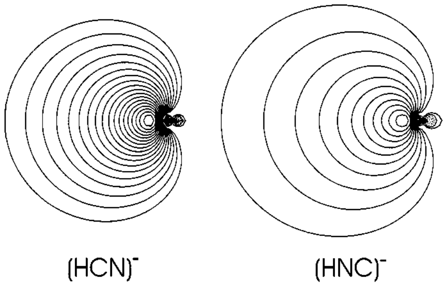

FIG. 1. Singly occupied molecular orbital for HCN^- (left) and HNC^- (right) (plotted with 0.000 14 contour spacing).

the static charge distribution of the neutral and (ii) allow for polarization and dispersion stabilization of the anion upon electron attachment. All the calculations of electron binding energies presented here were performed with the aug-cc-pVTZ basis set[33] supplemented with a $8s9p4d$ set of diffuse functions centered on the hydrogen atom (since this is at or near the centroid of the positive end of the dipole). The aug-cc-pVTZ basis set was chosen since we earlier showed its usefulness in describing dipole-bound anions compared to other commonly used one-electron basis sets.[34] The extra diffuse functions do not share exponent values and we used even-tempered[35] eight-term *s*, nine-term *p*, and four-term *d* basis sets. The geometric progression ratio was equal to 3.2,[36] and for each symmetry we started to build up the exponents of the extra diffuse functions from the lowest exponent of the same symmetry included in aug-cc-pVTZ basis set designed for hydrogen. As a consequence, we achieved the lowest exponents of 2.1106×10^{-6}, 2.6352×10^{-6}, and 6.3814×10^{-6} a.u., for the *s*, *p*, and *d* symmetries, respectively. The lowest eigenvalue of the atomic orbital overlap matrix was found to be 6.9×10^{-5} and 8.6×10^{-5} for HCN and HNC, respectively.

In computing correlation energies, all orbitals except the 1*s* orbitals of carbon and nitrogen were included. All calculations were performed with the GAUSSIAN98 program[37] on Intel Pentium III 500 MHz computers, and an SGI Origin2000 numerical server. The three-dimensional plots of molecular orbitals presented in Fig. 1, were generated with the MOLDEN program.[38]

In order to avoid erroneous results from the default direct SCF calculations with the basis sets with the large *s*, *p*, and *d* sets of diffuse functions, the keyword SCF =NoVarAcc was used and the two-electron integrals were evaluated (without prescreening) to a tolerance of 10^{-20} a.u.

III. RESULTS

A. Geometries of HCN and HNC at their minima and the minimum energy path for the HCN→HNC tautomerization

We optimized the geometries and calculated harmonic vibrational frequencies of the neutral HCN and HNC molecules at the QCISD level, and the resulting bond lengths and angles are collected in Table I (HCN and HNC are labeled $A0$ and $B0$ in this table). We then calculated the relative energies of both tautomers at the CCSD(T) level and we corrected them with corresponding zero-point vibrational energies. The CN bond is a very well-known triple bond in HCN while, after tautomerization, its order decreases so its length increases (from 1.15 Å for HCN to 1.17 Å for HNC). Both tautomers are linear ($C_{\infty v}$ symmetry) and HNC is higher in energy than HCN by 14.8 kcal/mol (14.4 kcal/mol when zero-point energy correction is included).

We also located the transition state (TS) corresponding to transfer of the hydrogen atom from C to N (its structure is labeled TS in Table I). Vibrational analysis confirms it is a first-order saddle point, and we estimate the kinetic barrier for the hydrogen transfer to be 32.8 kcal/mol at the CCSD(T) level (29.7 kcal/mol when zero-point energy terms are included).

The dipole moments for these three stationary points are very important since they indicate whether a stable dipole-bound anionic state can be formed at these geometries. We found SCF dipole moments values of 3.29, 2.87, and 1.31 Debye, for HCN, HNC, and the transition state structure, respectively. Thus, we expect weakly bound anion to exist at the HCN and HNC geometries but not for the TS.

The minimum energy path connecting HCN and HNC through the saddle point was determined at the QCISD level for the neutral system and is depicted on Fig. 2 while the geometrical parameters for eight geometries along this path ($A0$–$A4$ and $B0$–$B2$) having positive vertical electron attachment energies are collected in Table I.

B. Electron binding energies for HCN^- and HNC^- at their lowest energy geometries

Neither HCN nor HNC forms a valence-bound anion. However, the dipole moments calculated for these two conformers are larger than 2.5 Debye (see Table II), which suggests the possibility of binding an extra electron by the dipole potential to form stable dipole-bound anionic states. In this section we present detailed results for the linear $C_{\infty v}$-symmetry structures that correspond to minima on the ground-state potential-energy surface. The relevant rotational energy level spacings for these species are much smaller than the calculated values of D. Hence, non-BO coupling between the electronic and rotational degrees of freedom is expected to be of secondary importance for these anions and is not considered in this study.

The electron binding energy was partitioned into incremental contributions calculated at ‘‘successive’’ levels of theory [KT, SCF, MPn(n=2,3,4), and CCSD(T)], and the results for the optimal $C_{\infty v}$ structures of HCN and HNC are presented in Table II. In the KT approximation, the electron binding energy results from the electrostatic and exchange interactions of the loosely bound electron with the SCF charge distribution of the neutral molecule (primarily characterized by the dipole moment, but interactions with higher permanent multipoles and penetration effects are also included). For both systems, the D^{KT} values are very small: 11 cm^{-1} for hydrogen cyanide and only 3 cm^{-1} for the isocyanide tautomer. In line with this finding, it is also demonstrated in Fig. 1 that the singly occupied molecular orbital is much more diffuse for HNC^- than for HCN^-.

TABLE I. QCISD geometries and SCF dipole moments of the neutral structures on the HCN→HNC tautomerization path and electron binding energies of the corresponding dipole-bound anions [calculated at the KT, SCF, MP2, and CCSD(T) levels]. All the results calculated with aug-cc-pVTZ+$8s9p4d$ basis set. Bond lengths in Å, valence angles in degrees, dipole moments in Debyes, electron binding energies (D) in cm^{-1}. For description of the A and B symbols, see Fig. 2 and the text.

	Geometry	μ^{SCF}	D^{KT}	D^{SCF}	D^{MP2}	$D^{\mathrm{CCSD(T)}}$
$A0$ HCN (minimum)[a]	$r(\mathrm{CN})=1.154$ $r(\mathrm{HC})=1.065$ $\alpha(\mathrm{HCN})=180.00$	3.294	11.2	11.6	11.9	9.9
$A1$	$r(\mathrm{CN})=1.157$ $r(\mathrm{HC})=1.063$ $\alpha(\mathrm{HCN})=164.36$	3.230	9.2	9.4	9.6	7.7
$A2$	$r(\mathrm{CN})=1.176$ $r(\mathrm{HC})=1.026$ $\alpha(\mathrm{HCN})=164.69$	3.192	8.3	8.5	8.2	6.1
$A3$	$r(\mathrm{CN})=1.169$ $r(\mathrm{HC})=0.896$ $\alpha(\mathrm{HCN})=149.08$	2.839	2.1	2.2	2.1	1.1
$A4$	$r(\mathrm{CN})=1.162$ $r(\mathrm{HC})=1.101$ $\alpha(\mathrm{HCN})=133.09$	2.785	1.5	1.5	1.8	0.9
$B0$ HNC (minimum)[b]	$r(\mathrm{CN})=1.170$ $r(\mathrm{HC})=2.166$ $\alpha(\mathrm{HCN})=0.00$	2.866	3.2	3.3	13.2	42.5
$B1$	$r(\mathrm{CN})=1.175$ $r(\mathrm{HC})=2.080$ $\alpha(\mathrm{HCN})=11.05$	2.608	0.7	0.8	3.9	19.2
$B2$	$r(\mathrm{CN})=1.179$ $r(\mathrm{HC})=1.999$ $\alpha(\mathrm{HCN})=20.75$	2.365	0.05	0.06	0.9	6.6
TS (saddle point)[c]	$r(\mathrm{CN})=1.189$ $r(\mathrm{HC})=1.181$ $\alpha(\mathrm{HCN})=72.25$	1.310	⋯	⋯	⋯	⋯

[a] The corresponding QCISD vibrational frequencies for HCN are $\nu_1(\pi)=742$, $\nu_2(\pi)=742$, $\nu_3(\sigma)=2160$, $\nu_4(\sigma)=3459\,\mathrm{cm}^{-1}$, and the zero-point energy is 10.156 kcal/mol.

[b] The corresponding QCISD vibrational frequencies for HNC are $\nu_1(\pi)=465$, $\nu_2(\pi)=465$, $\nu_3(\sigma)=2081$, and $\nu_4(\sigma)=3843\,\mathrm{cm}^{-1}$, and the zero-point energy is 9.800 kcal/mol.

[c] The corresponding QCISD vibrational frequencies for TS are $\nu_1(a')=1192\,\mathrm{i}$, $\nu_2(a')=2021$, and $\nu_3(a')=2655\,\mathrm{cm}^{-1}$, and the zero-point energy is 6.684 kcal/mol.

The SCF binding energies include orbital relaxation and thus take into account static polarization of the neutral molecule by the extra electron and the secondary effect of back-polarization. In both cases, these contributions (which can be interpreted as orbital relaxation corrections to D^{KT}, denoted $\Delta D_{\mathrm{ind}}^{\mathrm{SCF}}$) are extremely small and are only 4% of the total D for HCN and are negligible for HNC. Although usually significant for valence-bound anions, orbital relaxation effects are usually negligible and rarely responsible for more than a few percent of the total value of D for the majority of dipole-bound anions studied so far.[27] Judging from the discrepancy between our results obtained with the valence double- and triple-zeta basis sets (the former not reported here), we ex-

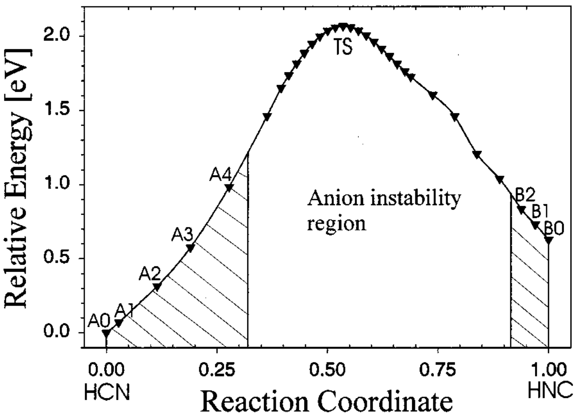

FIG. 2. The minimum energy path connecting HCN and HNC minima through the transition state obtained at the QCISD level.

TABLE II. The electron binding energies (in cm^{-1}) of HCN$^-$ and HNC$^-$ dipole-bound anions calculated with aug-cc-pVTZ+$8s9p4d$ basis set. Corresponding dipole moments (in Debye) calculated both from SCF and correlated (QCISD) densities.

	HCN$^-$	HNC$^-$
μ^{SCF}	3.29	2.87
μ^{QCISD}	3.05	3.08
D^{KT}	11.2	3.2
$\Delta D_{\mathrm{ind}}^{\mathrm{SCF}}$	0.4	0.1
$\Delta D_{\mathrm{disp}}^{\mathrm{MP2}}$	11.2	4.4
$\Delta D_{\mathrm{no\text{-}disp}}^{\mathrm{MP2}}$	−10.9	5.5
ΔD^{MP3}	−0.1	−3.4
ΔD^{MP4}	1.2	2.8
$\Delta D^{\mathrm{CCSD(T)}}$	−3.1	29.8
D^{total}	9.9	42.5

pect that our final CCSD(T) electron binding energies are converged to 2 cm^{-1}.

The contribution denoted $\Delta D_{\mathrm{disp}}^{\mathrm{MP2}}$ results from dynamical correlation between the loosely bound electron and the electrons of the neutral molecule. This stabilization is caused by quantum mechanical charge fluctuations, and is as large as D^{KT} (see Table II). This finding is consistent with our earlier results for other dipole-bound anions.[13] The value of $\Delta D_{\mathrm{disp}}^{\mathrm{MP2}}$ decreases from 11 cm^{-1} at the optimal geometry of HCN to 4 cm^{-1} at the optimal geometry of the HNC.

In addition to the dispersion interaction, other electron correlation factors may also affect the charge distribution (and dipole moment) of the neutral molecule and thus its electrostatic interaction with the extra electron. This effect first appears at the MP2 level and is denoted by $\Delta D_{\mathrm{no\text{-}disp}}^{\mathrm{MP2}}$. In the case of HCN, MP2 electron correlation effects reduce the dipole moment of the neutral system by 0.24 Debye in comparison with the SCF value, (see Table II). Therefore, the value of $\Delta D_{\mathrm{no\text{-}disp}}^{\mathrm{MP2}}$ is destabilizing, and the total MP2 contribution to D is small (0.3 cm^{-1}) but stabilizing due to the dominant role of the dispersion component. We observe a different situation in the case of the HNC tautomer where $\Delta D_{\mathrm{no\text{-}disp}}^{\mathrm{MP2}}$ is *stabilizing* and as large as $\Delta D_{\mathrm{disp}}^{\mathrm{MP2}}$. This can be easily explained by the fact that the dipole moment of the neutral HNC calculated from the SCF density is by 0.21 Debye *smaller* than when obtained from the correlated density (see Table II). Therefore both the dispersion and nondispersion terms are stabilizing and the total MP2 contribution to D is significant (10 cm^{-1}) and represents 23% of the total D.

The convergence of the MP series for the electron binding energy is satisfactory for HCN but problematic in the case of the HNC tautomer (see Table II). The contributions from ΔD^{MP3} are destabilizing but small for HCN yet significant for HNC. The contributions from ΔD^{MP4} are stabilizing and represent 12% and 6% of D, for HCN and HNC, respectively. Higher-order correlation effects, approximated here by $\Delta D^{\mathrm{CCSD(T)}}$ [the difference between CCSD(T) and MP4 binding energies], are different for the two systems studied. For HCN, this term is destabilizing which is surprising since we observed the opposite situation in the cases of dipole-bound anions studied thus far.[13] In the case of HNC, $\Delta D^{\mathrm{CCSD(T)}}$ is very large (30 cm^{-1}), stabilizing, and responsible for 70% of the net electron binding energy. By examining the HNC^{-} electron binding energy computed at the CCSD and CCSD(T) levels, we can estimate the contributions that triple excitations make; this analysis yields 14.4 cm^{-1}, which is a significant fraction of the total. Because the higher order contributions to the electron binding energy are large for HNC^{-} and because the triple excitations are treated only perturbatively [i.e., in CCSD(T)] at out highest level, our predictions for HNC^{-} should be viewed with greater doubt than for HCN^{-}. Nevertheless, combining all of our contributions produces our final predictions for the vertical electron attachment energies of 9.9 and 42.5 cm^{-1} for HCN and HNC, respectively.

We note that electron correlation effects represent 92% of the electron binding energy for the HNC^{-} anion. Even though this finding is consistent with our recent results for other dipole-bound species, where the correlation contributions were always crucial and very often responsible for more than 50% of the total value of D,[13] we find this contribution the largest of those described so far. Although the correlation effects represent more than 90% of the electron binding energy for HNC^{-}, it should be noted that this anionic bound state exists primarily due to the long range $\mu \cos \theta / r^2$ potential which causes localization of the excess electron on the positive side of the molecular dipole (see Fig. 1), as was recently discussed.[13] The case of HCN^{-} is also interesting since the correlation effects are destabilizing which is most likely caused by the fact that the electron binding energy is overestimated when calculated at the SCF level due to the overestimation of the dipole moment at this level.

C. Electron loss upon the $\mathrm{HCN}^{-} \rightarrow \mathrm{HNC}^{-}$ tautomerization

According to our findings, both HCN and HNC bind an excess electron very weakly at their minimum-energy geometries (by 10 and 43 cm^{-1}, respectively). This is primarily caused by the fact that these two molecules possess dipole moments slightly higher than the critical value needed to bind an excess electron. In order to determine whether the anion is stable near the transition state for HCN→HNC tautomerization, we calculated the dipole moment of the neutral system at the geometry of this saddle point. Since its value (1.31 Debye) is even smaller than the critical value (1.625 Debye) for binding to a point or fixed-finite dipole, we excluded the possibility of forming an electronically stable dipole-bound anionic state at this geometry.

These findings indicate that along the $\mathrm{HCN}^{-} \rightarrow \mathrm{HNC}^{-}$ tautomerization path the excess electron should autodetach. Thus, we next focused on determining approximately where along the minimum energy tautomerization path the electron loss occurs. To determine the stability of the anionic species along this path, we first calculated vertical attachment energies at the Koopmans' level for each point. We treated the negative eigenvalue of lowest unoccupied molecular orbital (LUMO) orbital for each structure as an indicator of a possible electronic stability of the anion and we performed a pair of CCSD(T) calculations (for neutral and anionic systems) in every such case.

Our results are shown in Fig. 2 where $A0$ and $B0$ indicate the HCN and HNC minima, respectively, and $A1-A4$, as well as $B1$ and $B2$ correspond to geometries at which the anion is bound (see also Table I). This allows us to shade the regions where the anionic species are stable which, not surprisingly, are localized close to both minimum energy structures (see Fig. 2).

We calculated the electron binding energies at the KT, SCF, MP2, and CCSD(T) level at every point where the anionic species is stable. Our results are collected in Table I and corresponding points on the tautomerization path are indicated in Fig. 2. Not surprisingly, the anion loses its excess electron close to the HNC^{-} minimum geometry but remains stable in a relatively large region in the vicinity of HCN^{-} minimum. The former is related to the fact that the KT electron binding energy of HNC^{-} is very small (3 cm^{-1}, see

Tables I and II). In the case of HCN^-, the larger electron binding energy allows the anion to preserve its stability much longer along the tautomerization path.

Analysis of the electron binding energies at the An and Bn geometries collected in Table I leads to another observation. For structure $B2$ on the tautomerization path (see also Fig. 2), the correlation contribution to the net electron binding energy is extremely large. The binding at the SCF level is very weak (0.06 cm^{-1}) but dramatically increases when electron correlation effects are taken into account. As a consequence, correlation effects are responsible for more than 99% of the total value of D. This situation is unusual because it illustrates an anion in which the excess electron is bound primarily by the interactions resulting from electron correlation. It should be noted, however, that the 1% of the binding brought by electrostatic-exchange interactions calculated at the KT level remains crucial for the existence of this anion since it allows the extra electron to be initially bound by the dipole potential of the neutral molecule.

The transfer of the hydrogen atom leading from HNC to HCN can be thought as a result of extreme excitation of the π bending vibration (see footer for Table I). Therefore, one can conclude that if the π bending vibration is excited sufficiently, the dipole moment of the system will not allow for binding an extra electron. For example, in the vicinity of the HNC^- minimum where the electron binding energy is small, we estimated that for $\nu_1(\pi)=465\,cm^{-1}$, excitation to the fifth excited level is enough to cause the detachment of the extra electron.

D. Is there a $H\cdots CN^-$ van der Waals complex?

Finally, we searched for a $H\cdots CN^-$ van der Waals complex that lies on the same energy surface as the HCN^- and HNC^- species that formed the main focus of this study. This aspect of our study is interesting because, in $H\cdots CN^-$, the extra electron occupies a valence orbital of the CN^- anion, whereas, in HCN^- it resides in a dipole-bound orbital. The evolution in character between valence and dipole-bound is one of the things we monitored along the path connecting the $H+CN^-$ and HCN^- structures.

We scanned the potential-energy surface for $H+CN^-$ at the CCSD(T)/aug-cc-pVTZ+($4s$, $4p$ diffuse) level. Not unexpectedly, we found that the H atom experiences stronger binding on the C than on the N side of CN^-. However, to our surprise, there seems to be no van der Waals minimum and hence no barrier separating such a complex from HCN^- as H approaches CN^- along a path from the C side of CN^- (n.b., we did not constrain the path to linear geometries). We note that it is not obvious that there must be a van der Waals minimum because there is no change in the dominant electronic configuration from the reactants $H+CN^-$ to the product HCN^-. In fact, we find that along such a path, the orbital in which the extra electron resides evolves smoothly from a CN^- based valence σ orbital to the dipole-bound orbital of HCN^-. Because of this smooth orbital evolution and because HCN^- lies far below $H+CN^-$, it appears that the sought-after van der Waals minimum (and the adjacent transition state) do not occur.

We also explored linear $H\cdots CN^-$ and $H\cdots NC^-$ structures and found stronger binding for the former with the H lying 2.13 Å from the C and with a C–N bond length of 1.177 Å. The basis set superposition corrected (BSSE) binding energy of this stationary point relative to $H+CN^-$ is 3.0 kcal/mol, and this linear $H\cdots CN^-$ is separated by a small barrier of 1.2 kcal/mol from the global minimum of HCN^-. However, this linear $H\cdots CN^-$ structure is not even a locally stable complex because our data suggest that it is unstable with respect to bending. Moreover, as we discuss in the preceding paragraph, the bent structure shows no local minimum as H approaches CN^-; instead, the energy evolves smoothly ''downhill'' until HCN^- is reached. So, we feel comfortable in suggesting that no linear or bent $H\cdots CN^-$ van der Waals complex exists. Even if future studies prove this conclusion wrong, we do not expect such a $H\cdots CN^-$ stationary point to be accessed in any experiment that studies HCN^- or HNC^- in low-lying vibrational levels because such a stationary point would lie ~40 kcal/mol higher than HCN^- and thus even above the transition state connecting HCN^- to HNC^-.

IV. CONCLUDING REMARKS

On the basis of CCSD(T)/aug-cc-pVTZ+$8s9p4d$ calculations we concluded that:

(i) HCN forms an electronically stable dipole-bound anion whose binding energy is 10 cm^{-1}.

(ii) HNC binds an extra electron by 43 cm^{-1} as a dipole-bound anion with a very large contribution (92%) of the electron correlation terms to the electron binding energy.

(iii) $HCN^-\rightarrow HNC^-$ isomerization for the anionic species should result in autodetachment of the excess electron since significantly bent structures cannot support a stable dipole-bound anion.

(iv) A $H\cdots CN^-$ van der Waals complex is unlikely to exist; instead $H+CN^-$ should evolve smoothly ''downhill'' to HCN^-.

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[1] T. Hirota, S. Yamamoto, K. Kawaguchi, A. Sakamoto, and N. Ukita, Astrophys. J. **520**, 895 (1999).
[2] S. D. Rodgers and S. B. Charnley, Astrophys. J. **501**, L227 (1998).
[3] T. J. Lee and A. P. Rendell, Chem. Phys. Lett. **177**, 491 (1991).
[4] B. Gazdy, D. G. Musaev, J. M. Bowman, and K. Morokuma, Chem. Phys. Lett. **237**, 27 (1995).
[5] W. Jakubetz and B. L. Lan, Chem. Phys. **217**, 375 (1997).
[6] (a) F. J. Adrian, E. L. Cochran, V. A. Bowers, and B. C. Weatherley, Phys. Rev. **177**, 129 (1969); (b) S. Tsuda, A. Yokohata, and T. Umaba, Bull. Chem. Soc. Jpn. **44**, 1486 (1971).
[7] J. Pacansky, N. S. Dalal, and P. S. Bagus, Chem. Phys. **32**, 183 (1978).

[8] L. L. Lohr, J. Phys. Chem. **89**, 3465 (1985).
[9] W. R. Garrett, Chem. Phys. Lett. **62**, 325 (1979).
[10] W. R. Garrett, J. Chem. Phys. **71**, 651 (1979).
[11] K. D. Jordan and J. J. Wendoloski, Chem. Phys. **21**, 145 (1977).
[12] T. Koopmans, Physica (Amsterdam) **1**, 104 (1934).
[13] M. Gutowski and P. Skurski, Recent Res. Devel. Physical Chem. **3**, 245 (1999).
[14] P. Skurski, M. Gutowski, and J. Simons, J. Chem. Phys. **110**, 274 (1999).
[15] P. Skurski, M. Gutowski, and J. Simons, J. Phys. Chem. A **103**, 625 (1999).
[16] E. Fermi and E. Teller, Phys. Rev. **72**, 399 (1947); A. S. Wightman, *ibid.* **77**, 521 (1949); J. E. Turner, V. E. Anderson, and K. Fox, *ibid.* **174**, 81 (1968).
[17] H. O. Crawford, Proc. R. Soc. London **91**, 279 (1967).
[18] H. O. Crawford and A. Dalgarno, Chem. Phys. Lett. **1**, 23 (1967).
[19] K. D. Jordan and W. Luken, J. Chem. Phys. **64**, 2760 (1976).
[20] W. R. Garrett, J. Chem. Phys. **77**, 3666 (1982).
[21] M. Gutowski, P. Skurski, A. I. Boldyrev, J. Simons, and K. D. Jordan, Phys. Rev. A **54**, 1906 (1996).
[22] M. Gutowski, P. Skurski, J. Simons, and K. D. Jordan, Int. J. Quantum Chem. **64**, 183 (1997).
[23] M. Gutowski and P. Skurski, J. Phys. Chem. B **101**, 9143 (1997).
[24] P. Skurski and M. Gutowski, J. Chem. Phys. **108**, 6303 (1998); M. Gutowski, K. D. Jordan, and P. Skurski, J. Phys. Chem. A **102**, 2624 (1998).
[25] D. M. A. Smith, J. Smets, Y. Elkadi, and L. Adamowicz, Pol. J. Chem. **72**, 1615 (1998).
[26] Y. Elkadi and L. Adamowicz, Chem. Phys. Lett. **261**, 507 (1996).
[27] G. L. Gutsev and R. J. Bartlett, J. Chem. Phys. **105**, 8785 (1996).
[28] D. M. A. Smith, J. Smets, Y. Elkadi, and L. Adamowicz, J. Chem. Phys. **107**, 5788 (1997).
[29] G. L. Gutsev and L. Adamowicz, J. Phys. Chem. **99**, 13412 (1995).
[30] J. A. Pople, M. Head-Gordon, and K. Raghavachari, J. Chem. Phys. **87**, 5968 (1987).
[31] R. J. Bartlett and J. F. Stanton, in *Reviews in Computational Chemistry*, edited by K. B. Lipkowitz and D. B. Boyd (VCH, New York, 1994), Vol. V.
[32] P. R. Taylor, in *Lecture Notes in Quantum Chemistry II*, edited by B. O. Roos (Springer-Verlag, Berlin, 1994).
[33] R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
[34] P. Skurski, M. Gutowski, and J. Simons, Int. J. Quantum Chem. **80**, 1024 (2000).
[35] M. W. Schmidt and K. J. Ruedenberg, Chem. Phys. **71**, 3961 (1979).
[36] M. Gutowski and J. Simons, J. Chem. Phys. **93**, 3874 (1990).
[37] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN98, Revision A.7, Gaussian, Inc., Pittsburgh PA, 1998.
[38] G. Schaftenaar and J. H. Noordik, MOLDEN: a pre- and post-processing program for molecular and electronic structures, J. Comput.-Aided Mol. Design **14**, 123 (2000).