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Dipole-bound anionic state of nitromethane. *Ab initio* coupled cluster study with first-order correlation orbitals

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The theoretical procedure based on the coupled cluster method and the first-order correlation orbital for studying dipole-bound states of polyatomic molecules is presented. The calculation of the lowest dipole-bound state for the nitromethane molecule indicates that the molecular dipole of this molecule, which is experimentally known to be 3.46 D, can attract an extra electron with the energy of 0.000 127 hartree and form a bound state. This state should be considered as a short-living intermediate leading to the formation of a stable valence-bound anion.

I. INTRODUCTION

Dipole-bound electronic states of molecules, long predicted by theoretical calculations,[1] was recently observed by means of ultrahigh-resolution photodetachment spectroscopy by Maed, Lykke, Lineberger, Marks, and Brauman[2] for the acetaldehyde enolate negative anion. The existence of such novel states, where the extra electron is bound primarily by infraction with the electric dipole moment of the neutral core, has been suggested by a number of experiments. An example of this would be the detection of strong resonances near-zero energy by Wong and Schulz,[3] and Rohr and Linder.[4] However, more convincing experimental evidence for dipole states resulted from low-resolution photodetachment studies of highly polar negative anions conducted by Brauman *et al.*[5]

On the theoretical side there have been numerous calculations of both ground end excited states of dipole-bound anions. A pioneer in this area was Jordan and collaborators.[6] Our interest in this area was directed to the development of new theoretical tools for calculating anionic ground and excited dipole-bound states of polar diatomic systems using numerical orbital techniques[7] in conjunction with the MCSCF method,[8] the coupled cluster (CC) method and the many-body perturbation theory (MBPT).[9] The present work is a continuation of this effort and addresses dipole-bond states of polyatomic systems.

It was demonstrated by Garrett[10] that a theoretical methodology based on the Born–Oppenheimer (BO) approximation might be inaccurate for calculating the attachment energy into the dipole-bound state, especially when this energy approaches or becomes smaller than the value of the molecular rotation constant. When this happens, the rotational motion of the molecule becomes closely correlated with the orbital motion of the dipole-bound electron and, consequently, a non-BO treatment is necessary to describe the attachment process. However, for the majority of the larger polyatomic molecules whose dipole moments exceed 3 D the lowest dipole states can be studied with conventional BO techniques due to their sizable rotational constants, and this is the approach taken here.

There are numerous polyatomic systems, some of them of biological significance, whose dipole moment suffices to support an extra electron in the bound state. The formation of such states could provide a bridge for more complex electron transfer reactions which eventually lead towards formation of more stable anions. It was suggested[11] that the dipole states are indeed short-lived excited anionic states that undergo deexcitation to "valence" anionic states, which incorporate the extra electron in a valence shell rather than in a diffused dipole-supported orbital. An example of such a mechanism is an electron captured by the acetaldehyde enolate molecule, which proceeds through a formation of an excited anionic state with all the characteristics of a weakly bound dipole-bound state, and eventually converges to a stable valence state of the enolate negative anion.[11] One may expect the same mechanism for an electron attachment to the nitromethane molecule which possesses a sizable dipole moment of 3.46 D[12] and also forms a stable valence-bound negative anion.[13]

It was experimentally established that the structure of the "neutral core" for the dipole-bound anion of acetaldehyde enolate is virtually identical as in the neutral system.[2] This is obviously a result of the diffused character of the orbital carrying the extra electron. The size of this orbital was estimated for about 100 Å^2 in agreement with our calculation of the average core-electron separations for dipole-bound states of polar diatomics.[9]

II. METHODOLOGY

One may encounter the following difficulties in theoretical calculations of dipole-bound states for polyatomic molecules by means of *ab initio* quantum chemical methods based on the Born–Oppenheimer approximation:

(i) The very diffused character of the dipole state mandates diffused basis functions which are different from what

one usually employs for the neutral systems or even for conventional valence-bound anions.

(ii) The energy and the wave function for the extra electron is very sensitive to the size of the molecular dipole moment. It is, therefore, essential to calculate the molecular neutral core at the level of the theory which correctly describes the electronic distribution and, consequently, produces the dipole moment in agreement with the experiment. The well-known deficiency of the SCF method in correctly reproducing the molecular dipole moment makes this method inadequate for the present purpose.

(iii) The electron affinity corresponding to the dipole state is predominantly determined by the electrostatic interaction. There is, however, a sizable contribution for the correlation effect between the extra electron and the core electrons which has to be accounted for.[8] Besides the basis set problem which such a calculation may create, it is essential to employ a size-extensive method[14] which correctly scales with the number of electrons. This is especially important when the electron attachment energy is calculated as a difference between the energy of the anion and the neutral system, which obviously differ in the number of electrons. This seems to favor perturbation approaches such as MBPT or the coupled-cluster methods over the variational approaches such as CI.

(iv) Unlike the polar diatomics, where the dipole-electron model for the anion formation works quite well, the formation of the polyatomic dipole-bound state is probably more complex. Besides the primary dipole-electron interaction, this process may possibly also involve localizations of the charge density of the extra electron in domains of positive potential appearing in various places in the molecule. The resulting state is, thus, not a pure dipole-bound state but also has some "valence" contributions, which have to be anticipated when the basis-set selection is made.

In the view of the above, we propose the following procedure for calculating the electron affinity of the lowest dipole-bound state of a polyatomic molecule, which we shall then apply to determine the electron affinity of nitromethane. The procedure is described as applied to the nitromethane dipole-bound state.

A. Basis set selection

The calculations for the nitromethane molecule and the dipole-bound nitromethane anion were done using the optimized SCF geometry of the neutral molecule[15] and the same basis sets, which are comprised of the following groups of functions:

(a) Standard Gaussian DZP basis taken from Dunning and Hay[16] for carbon, nitrogen, oxygen, and hydrogen, and augmented by a set of polarization functions for each atom with exponents taken from Redmon et al.[17]

(b) A set of diffused s and p Gaussian functions with exponents 0.034, 0.048, and 0.059 for carbon, nitrogen, and oxygen respectively.

(c) Three sets of s,p functions (a total of 12 primitive Gaussian orbitals) which were placed in the geometrical center of the triangle formed by the three hydrogen nuclei.

Our previous numerical Hartree–Fock calculations on dipole-bound states of several polar diatomic molecules and subsequent mapping of the numerical orbitals on a set of Slater functions[18] indicated that at least two sp shells are needed to describe such states. The exponents of the Gaussian functions were optimized by the minimization of the orbital energy of the first unoccupied (virtual) SCF orbital for the neutral molecule. A similar Koopmans-theorem-based approach was applied by Wendolski and Jordan.[6] The exponent optimization was performed in an even-tempered fashion by restricting the three exponents to form a geometrical series, $\alpha^i\beta$ $i = 1,2,3$ ($\alpha = 0.1$), and varying only the multiplier β. The optimal value of β was found to be approximately 0.2, yielding the values of the exponents for the three sets of s,p Gaussians equal to 0.02, 0.002, and 0.0002, respectively.

The total number of basis functions in our calculations was equal to 103. Obviously, there still exists a possibility of a basis set incompleteness, but the above basis should suffice to account for the most important effects involved in the anion formation, including the correlation of the electrons of the neutral core, the formation of the lowest anionic dipole-bound state with a possible valence-bound contribution, and the correlation of the extra electron with core electrons.

B. SCF calculation–reference wave-functions

The SCF calculation of the neutral molecule yielded the results presented in Table I. According to Koopmans theorem, the first unoccupied orbital in the a' symmetry with negative near-zero energy corresponds to the lowest dipole-bound state. The reference wave function for the anion was constructed from the SCF Slater determinant for the neutral by placing the additional electron into this "Koop-

TABLE I. Determination of the electron affinity of the dipole-bound states of the nitromethane molecule. All energies in a.u.

	CH_3NO_2		$CH_3NO_2^-$
SCF/reference wave function	− 243.719 093		− 243.719 309
Orbital symmetry distribution	a'	a''	
full space	74	29	
occupied orbitals	13	3	
virtual orbitals	61	26	
FOCOs	17	7	
FOCO generation			
E_2 (full space)	− 0.685 988		
E_2 (24 FOCOs)	− 0.527 508		
Coupled cluster calculation (CCSD)			
correlation energy	− 0.538 159		− 0.538 069
total energy	− 244.257 252		− 244.257 379
largest CC amplitudes:			
single excitation ($a'' \to a''$)	− 0.043 683		− 0.043 338
double excitation ($a'' \to a''$)	− 0.116 305		− 0.115 988
Electron affinity			
Koopmans' theorem	0.000 216		
CCSD	0.000 127		

mans orbital." The electron affinity calculated as the difference between the total energies corresponding to the reference wave functions for the neutral and anionic systems is obviously equal to the orbital energy of the Koopmans orbital of 0.000 216 hartree. Although the anionic reference wave function is not generated in a direct SCF calculation for the anion but through the Koopmans approximation, it should provide a rather good representation of the anionic state considering a very small perturbation of the core electrons due to an additional electron located in a very diffused orbit.

C. Correlation of core electrons

For the same reason as mentioned above, one may anticipate that the correlation contributions of the core electrons in the wave functions of the neutral molecule and the anion are similar and would require a similar orbital space to form the configuration expansion representations. The set of the core correlation orbitals was, therefore, obtained for the neutral system and used for both the neutral and the anion. We used our first-order correlation orbital (FOCO) procedure for the orbital generation.[19] This procedure provides an optimization scheme for the contraction coefficients of the SCF virtual orbitals to form a compact set of correlation orbitals which is much shorter than the SCF virtual set, and therefore better suited for a high-order correlation calculation whose computational time usually depends dramatically on the number of correlation orbitals. Prior to the optimization, a subset of nine orbitals with the lowest orbital energies was excluded from the virtual set. These diffused orbitals, which are almost exclusively linear combinations of the nine s,p Gaussians positioned between the hydrogen nuclei of the CH_3 group, are eventually added to the orbital set in the final coupled cluster calculations for the neutral and anionic systems. There were two purposes for excluding the diffused orbitals from the FOCO step but including them in the final CC calculations. The first purpose was to provide an adequate functional space for a possible adjustment of the spatial distribution of the extra electron which can result from including the correlation effects of the core electrons. The second purpose was to account for the correlation effects between the extra electron and the core electrons, which usually require functions as diffused as the Koopmans' orbital itself.

The remaining 78 virtual orbitals were used next to optimize a set of 24 FOCOs by the minimization of the second-order Hylleraas functional, which constitutes an upper bound to the second-order correlation energy:

$$E_2 \leqslant \langle \Phi_0 | H_0 - E_0 | \Phi_0 \rangle + 2\langle \Phi_0 | H - H_0 | \Phi_1 \rangle , \qquad (1)$$

where the unperturbed Hamiltonian H_0 is defined as the sum of the Fock operators; Φ_0 and E_0 are the Hartree–Fock wave function and the energy, respectively, and Φ_1 is the first-order correlation wave function. The FOCO optimization is accomplished by separating the virtual set into an active and nonactive set, expressing the unitary transformation U between the active and nonactive orbitals in an expo-

nential form with a antisymmetric matrix R,

$$U(R) = \exp(R) ,$$
$$R = -R^\dagger , \qquad (2)$$

and minimizing the Hylleraas functional determined with the active orbitals by varying the elements of the matrix R. The number of FOCOs was chosen arbitrarily to be equal to twice the number of the occupied orbitals (eight $1s$ electrons were not correlated), which is usually sufficient to capture the major portion of the second-order correlation energy.[20] Indeed, for the nitromethane molecule with 24 FOCOs we got about 77% of the second-order result determined with all 87 virtual orbitals (see Table I). The symmetry distribution of FOCOs (17 and 7 in symmetries a' and a'', respectively) was decided based on the highest occupancies of the approximate natural orbitals determined through the diagonalization of the second-order density matrix.

The final set of orbitals to be used in subsequent correlation calculations comprised the 16 SCF occupied orbitals for the neutral nitromethane, $\{i\}$, $i = 1,...,16$, the 9 diffused virtual orbitals, $\{x\}$, $x = 1,...,9$, which include the virtual orbital being the Koopmans approximation for the lowest dipole state, and the 24 FOCOs for the correlation of the valence electrons of the neutral system, $\{a\}$ $a = 1,...,24$.

D. Coupled cluster calculations on the neutral and anionic nitromethane

We employed the coupled cluster method with single and double excitations (CCSD) to perform calculations on the nitromethane molecule and the nitromethane anion using the reference wave functions described above. In the spin-orbital notation, the CC neutral and anionic wave functions have the following forms:

$$\Psi_N = \exp(\widehat{T}_1 + \widehat{T}_2)|i_1\bar{i}_1\cdots i_{16}\bar{i}_{16}| , \qquad (3)$$
$$\Psi_A = \exp(\widehat{T}_1 + \widehat{T}_2)|i_1\bar{i}_1\cdots i_{16}\bar{i}_{16}x_1| , \qquad (4)$$

where the coupled cluster operators are the following expansions in terms of spin-orbital creation and anihilation operators:

$$\widehat{T}_1 = \sum_{k,p} t_k^p a_p^\dagger a_k ,$$

$$\widehat{T}_2 = \sum_{\substack{k>k' \\ p>p'}} t_{kk'}^{pp'} a_p^\dagger a_k a_{p'}^\dagger a_{k'} ,$$

and the spin-orbital domains are defined as follows:
for the neutral molecule,

$$\{k\} = \{i,\bar{i}\} ,$$
$$\{p\} = \{x,\bar{x}\} \cup \{a,\bar{a}\} ;$$

and for the anion,

$$\{k\} = \{i,\bar{i}\} \cup \{x_1\}$$
$$\{p\} = \{x,\bar{x}\} \cup \{a,\bar{a}\} - \{x_1\} .$$

The CC calculations were accomplished with the PROPAGATOR program system,[21] and the spin-restricted regime was assumed for the neutral (close shell singlet) and the spin-

unrestricted regime for the anion (doublet state). Even though the reference anionic wave function had the same spatial orbitals for electrons with α and β spins, the iterative process of the CC method produced some spin polarization of the core electrons as a result of the interaction with the extra single α electron position in the Koopmans orbital. Another task of the CC method in the anionic calculation besides the primary one—correlating the electrons—was to account for the relaxation of the core charge distribution in the electric field created by the additional electron. This relaxation would be incorporated in the reference function if the CC calculation were performed, based on the UHF wave function for the anion. However, such a wave function would be difficult to generate considering that it does not correspond to the ground anionic state. In the calculation for the neutral system, there was no need for the spin polarization or for the charge relaxation.

The correlation effects produce noticeable changes in the neutral and anionic wave functions. These changes exhibit themselves in the size of the CC amplitudes, especially those corresponding to the double excitations. Upon examining these amplitudes (see Table I), one sees that for both wave functions the largest values (about 0.12) belong to the same double excitation from a valence a'' orbital to a correlation orbital of the same symmetry. This excitation is primarily responsible for the alternation of the dipole moment of the neutral core. The single excitations are much less important. Worth noticing are the rather small amplitudes for excitations from the Koopmans orbital holding the extra electron in the anionic calculation, indicating that the correlation-induced dipole moment change does not drastically change the structure of the dipole-attached electron.

For the present calculations we used the SCS-40 minisupercomputer located in the University of Arizona Computer Center. The cumulative computer time for the anion was about 9 h, double the amount required by the spin-restricted calculation for the neutral. The convergence of the CC iterative procedure was fast in both cases, which is what has always been observed in all CC calculations utilizing the FOCOs.

III. RESULTS AND DISCUSSION

The electron affinity of a dipole-bound state strongly depends on the size of the molecular dipole moment. For the nitromethane molecule, the SCF dipole moment obtained in our calculation, which is equal to 4.35 D is almost 1 D larger than the experimentally established value of 3.46 D. However, the value of the dipole moment calculated at the lowest correlated level [MBPT(2)], equal to 3.61 D, already resembles the experimental result much better. One may, therefore, expect that the electron affinity of 0.000 216 hartree based on the Koopmans theorem determination is definitely too high. However, at the CC level of theory, which more adequately reproduces the dipole moment of the neutral core, the electron affinity should become smaller and more realistic. Indeed, our CC calculation produced a result of 0.000 127 a.u. (see Table I), which is significantly smaller

than the Koopmans value. No experimental results are yet available for verification.

The present procedure for calculating electron affinities of the dipole-bound states can be applied to larger molecules with sizeable dipole moments such as substituted benzenes or pirimidines which exhibit relatively large dipole moments. High-level theoretical treatment of such systems with extended basis sets is now enabled by the FOCO procedure. Studies of the dipole-bound states may lead to a better understanding of the formation of stable valence anionic states of complex molecules, which proceed through the dipole intermediates.

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