PHYSICAL REVIEW A VOLUME 58, NUMBER 6 DECEMBER 1998

BRIEF REPORTS

Brief Reports are accounts of completed research which do not warrant regular articles or the priority handling given to Rapid Communications; however, the same standards of scientific quality apply. (Addenda are included in Brief Reports.) A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.

Two thermodynamically stable states in SiO^- and PN^-

Gennady L. Gutsev and Puru Jena
Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000

Rodney J. Bartlett
Quantum Theory Project, P.O. Box 118435, University of Florida, Gainesville, Florida 32611-8435

(Received 6 July 1998)

In contrast to the well-known CO and N_2 molecules, isoelectronic SiO and PN form thermodynamically stable conventional (valence) and dipole-bound anion states upon attachment of an extra electron. According to the results of our high-quality *ab initio* calculations, binding energies of the electron in these states are 38 and 1.6 meV (SiO^-) and 76 and 1.0 meV (PN^-), respectively. Dissociation trends of the SiO^- and PN^- anions are discussed. [S1050-2947(98)01312-2]

PACS number(s): 03.65.Ge, 31.10.+z, 31.15.Ar, 31.25.−v

The SiO and PN molecules are isoelectronic to each other as well as to the CO and N_2 molecules. The latter pair are known not to form thermodynamically stable anions but exhibit wide low-energy resonance structures in electron-scattering experiments [1], which appear to reflect attachment of an extra electron to higher vibrational states of the ground-state CO and N_2 molecules [2]. Unlike CO, whose dipole moment is 0.112 D [3], and N_2, having no permanent dipole moment at all, SiO and PN possess rather sizable dipole moments of 3.0982 D [4] and 2.7564 D [5], respectively. Such magnitudes of the dipole moment should be sufficient for sustaining dipole-bound states (DBSs) of the SiO^- and PN^- anions because extensive experimental and computational studies [6,7] of an extra electron attachment to a number of polar organic molecules have shown the critical value of the dipole moment required to support a DBS to be 2.5 D.

Both SiO^- and PN^- have been observed in mass spectra [8,9] and the electron affinity of PN was estimated in 0.32 ± 0.20 eV [9]. No experimental estimate has been obtained for the SiO electron affinity, to the best of our knowledge. *Ab initio* computations [10,11] performed with moderate-size basis sets failed to prove the existence of SiO^-.

A proper theoretical description of weakly bound anion states is known to require the use of large basis sets containing very diffuse functions and an accurate account of the electron correlation [12]. Therefore, for a search of stable SiO^- and PN^- states, we applied a rather reliable level theory, namely, the infinite-order coupled-cluster method with all singles and doubles (CCSD) and noniterative inclusion of all triple excitations CCSD(T) [13,14] in conjunction with a large atomic natural orbital basis of Widmark, Malm-

TABLE I. Spectroscopic constants and total energies of the SiO-SiO^- (top) and PN-PN^- (bottom) pairs computed at the CCSD(T) level together with experimental data. Equilibrium bond lengths R_e are in Å, rotational constants B_e are in cm^{-1}, harmonic vibrational frequencies ω_e are in cm^{-1}, dipole moments μ are in debyes, total energies are in hartrees, and adiabatic electron affinities A_{ad} and vertical detachment energies E_{VD} are in eV.

Property	SiO, $^1\Sigma^+$ This work	SiO, $^1\Sigma^+$ Expt.[a]	SiO^-, $^2\Pi$ This work
R_e	1.5130	1.5097	1.5545
B_e	0.723 58	0.726 75	0.685 52
ω_e	1242.4	1241.5	1080.8
μ	3.0971	3.0982	
E_{tot}	−364.424 016		−364.425 033
	$A_{ad}=0.038$		$E_{VD}=0.083$

Property	PN, $^1\Sigma^+$ This work	PN, $^1\Sigma^+$ Expt.[a]	PN^-, $^2\Pi$ This work
R_e	1.4927	1.4911	1.5447
B_e	0.784 55	0.7862	0.732 62
ω_e	1342.7	1337.2	1145.0
μ	2.7680	2.7465	
E_{tot}	−395.775 617		−395.777 513
	$A_{ad}=0.076$	0.32 ± 0.20	$E_{VD}=0.154$

[a] Spectroscopic constants are from Ref. [24]; permanent dipole moments of SiO and PN are from Refs. [4] and [5], respectively; and the electron affinities of PN are from Ref. [9].

1050-2947/98/58(6)/4972(3)/$15.00

qvist, and Roos [15]. This basis consists of $14s9p4d3f$ and $17s12p5d4f$ sets of primitive Gaussian-type orbitals for N,O and Si,P, contracted to $7s7p4d3f$ and $7s7p5d4f$ sets, respectively. Computations are performed with the ACES II suite of programs [16].

The results of our calculations for the SiO-SiO$^-$ and PN-PN$^-$ pairs, presented in Table I, are in accord with experimental data. The $^2\Pi$ states of SiO$^-$ and PN$^-$ are lower in the total energies than the $^1\Sigma^+$ ground states of SiO and PN, respectively, which testifies of the existence of thermodynamically stable states of SiO$^-$ and PN$^-$. An analysis of T_1 and T_2 amplitudes, which are indicative of a multiconfigurational nature of wave functions, has shown that the largest amplitude does not exceed 0.05 in all cases. This testifies of the essentially one-determinant character of anionic and neutral states near the corresponding equilibrium geometries.

The binding energy of an extra electron in a particular anion state is defined as the difference in the total energies of the anion and its neutral parent states. The adiabatic electron affinity $A_{\rm ad}$ measures the binding energy of an extra electron in the ground state of an anion with respect to its ground-state neutral parent. Within the Born-Oppenheimer (BO) approximation, employed in the present work, $A_{\rm ad}$ can be estimated as

$$A_{\rm ad}=E_{\rm tot}(N,R_e)+Z_N-E_{\rm tot}(A,R_e^-)-Z_A=\Delta E_{\rm el}^{\rm ad}+\Delta E_{\rm nuc}, \tag{1}$$

where R_e and R_e^- denote equilibrium bond lengths of a neutral molecule N and its anion A, respectively. The zero-point vibrational energy Z is computed within the harmonic approximation.

The vertical detachment energy $E_{\rm VD}$ of an extra electron from an anion can be defined within the BO approximation as

$$E_{\rm VD}=E_{\rm tot}(N,R_e^-)+Z_N-E_{\rm tot}(A,R_e^-)-Z_A=\Delta E_{\rm el}^{\rm VD}+\Delta E_{\rm nuc}. \tag{2}$$

The vertical attachment energy $E_{\rm VA}$ gained by a neutral molecule upon a sudden attachment of an extra electron is defined in a similar manner

$$E_{\rm VA}=E_{\rm tot}(N,R_e)+Z_N-E_{\rm tot}(A,R_e)-Z_A=\Delta E_{\rm el}^{\rm VA}+\Delta E_{\rm nuc}. \tag{3}$$

Since one can expect a rather small change in the nuclear energy due to low-amplitude displacements around the equilibrium geometry, one can use the Z_N and Z_A evaluated from harmonic frequency calculations at R_e and R_e^-, respectively. So we consider $\Delta E_{\rm nuc}$ to be the same in Eqs. (1)–(3).

The $A_{\rm ad}$'s of SiO and PN computed according to Eq. (1) are 38 and 76 meV, respectively, which is consistent with insignificant elongations of the bond lengths due to attachment of an extra electron (by approximately 0.05 Å in both cases). As follows from the results of *ab initio* calculations [6,17–19] and experimental measurements [7], dipole moments of about 3 D are able to sustain DBSs with binding energies of 1–2 meV. Dipole moments in excess of 10 D appear to be required [18] for supporting Π-type DBSs. Only totally symmetric DBSs have been found for polar systems possessing smaller dipole moments by now. Therefore, the $^2\Pi$ states of SiO$^-$ and PN$^-$ should be attributed to conventional valence-type states, which would mean that the anions could possess additional dipole-bound states of Σ symmetry.

In order to properly describe very diffuse charge distributions corresponding to dipole-bound electrons, one needs to augment a standard basis set by sufficiently diffuse functions. We follow the same procedure as before [18,20] having added a set of diffuse functions consisting of seven *sp* shells (the exponents are 0.001, 0.0005, 0.0001, 0.000 05, 0.000 01, 0.000 005, and 0.000 001) to the Widmark-Malmqvist-Roos (WMR) basis and placed them at the distance of 3 Å beyond the Si and P atoms along the molecular axes (i.e., in the direction of the positive end of the dipole).

Since attachment of an extra electron to a polar molecule resulting in the formation of a DBS does not lead to any appreciable change in the geometry [6,21], one can compute the binding energy of an extra electron as the vertical attachment energy defined by Eq. (3) at the equilibrium geometry of the neutral parent. In such a case, the $E_{\rm VA}$ is identical to the $E_{\rm VD}$ defined by Eq. (2).

A convenient way for the $E_{\rm VA}$ calculations presents the electron-attachment equation-of-motion coupled-cluster (EAEOMCC) method [22,23], which treats simultaneously a number of states having one more electron than an initial parent state. The parent state is described at the CCSD level as

$$|\Psi_{\rm CCSD}\rangle=e^{\hat{T}}|\Phi_0\rangle, \tag{4}$$

where $|\Phi_0\rangle$ is a reference Hartree-Fock (HF) wave function and $\hat{T}=\hat{T}_1+\hat{T}_2$ is the cluster operator limited to single and double excitations. The transformed Hamiltonian is defined as

$$\bar{\hat{H}}=e^{-\hat{T}}\hat{H}e^{\hat{T}} \tag{5}$$

and $\bar{\hat{H}}-E_{\rm CCSD}$ is diagonalized over a suitable set of configurations. These configurations comprise all one-particle $(1p)$ and two-particle–one-hole $(2p1h)$ determinants describing states with an extra electron attached. Final states are linear combinations

$$\left(\sum_a c_a a^\dagger+\sum_{a,b,j} c_{a,b}^j a^\dagger b^\dagger j\right)e^{\hat{T}}|\Phi_0\rangle, \tag{6}$$

where $a^\dagger,b^\dagger$ denote creation operators for unoccupied orbitals (particles), j is an annihilation operator for orbital j (hole) occupied in the reference Φ_0 state, and c_a and $c_{a,b}^j$ are amplitudes. The eigenvalues obtained from the diagonalization are the vertical attachment energies with respect to the CCSD reference state.

According to the results of our EAEOMCC calculations performed with the augmented WMR basis at the neutral equilibrium geometries, binding energies of an extra electron in dipole-bound states of SiO$^-$ and PN$^-$ are 1.6 and 1.0 meV, respectively. The attached electron fills in a σ-type molecular orbital of the reference wave functions, so the resulting anion states have $^2\Sigma^+$ symmetry. A smaller binding energy in PN$^-$ with respect to SiO$^-$ is consistent with the larger dipole moment of SiO.

Jordan and Luken [25] have proposed that different dipole-bound states of the $LiCI^-$ anion can develop in different dissociation channels of the anion upon the bond length stretching. Having taken the LiH^- anion as an example, we have shown [20] that dipole-bound states can be temporary, namely, appear at bond lengths where the dipole moment of a neutral parent increases enough and decay at large internuclear separations where the dipole moment drops down below 2.5 D. It should happen since the ground-state neutral molecule dissociates to electroneutral atoms.

The Si atom can form three different states upon attachment of an extra electron: P^- and O^- have a single stable state each and N is known not to attach an extra electron at all [26]. Therefore, one should expect four dissociation channels for the SiO^- anion and one for the PN^- anion. However, both of them have two thermodynamically stable states, which means that the anions have different behavior at larger internuclear separations. The dipole state of PN will decay at bond lengths where the dipole moment becomes to be lower than approximately 2.5 D or, in other words, its dissociation limit is $P+N+e$, whereas the valence state decays to P^-+N.

In order to have a notion about the SiO^- behavior while the Si-O bond stretches, we performed a series of EAEOMCC calculations at bond lengths ranging from 1.7 to 2.5 Å. At larger distances, the restricted HF-based calculations appear to be unreliable since the restricted HF solution has a Si^-+O^+ asymptotic limit instead of the correct Si+O one. Similar to the LiH case, the dipole moment of SiO increases up to $R(\text{Si-O})\approx 2.5$ Å, in agreement with the results of Langhoff and Bauschlicher's calculations [27]. This reflects the change in the bonding type from covalent to ionic before dissociation. The second dipole-bound state of SiO^- appears at $R(\text{Si-O})\approx 2.2$ Å, where the dipole moment increases to 4.8 D, and the third dipole bound state appears at $R(\text{Si-O})\approx 2.5$ Å, where the dipole moment of SiO increases up to approximately 5.3 D. Thus two additional dipole-bound states of SiO^- are temporary: They appear at large bond elongations and correspond to decay channels $O+Si^{-*}$ or Si^{-**}.

This work was partially supported by the Office of Naval Research, Grant No. N00014-95-1-0614, and the Department of Energy (Grant No. DE-FG05-87ER45316). We appreciate helpful discussions with Dr. Alexander Boldyrev.

[1] G. J. Schulz, Rev. Mod. Phys. **45**, 423 (1973).

[2] G. L. Gutsev, P. B. Rozyczko, R. J. Bartlett, and C. A. Weatherford (unpublished).

[3] *CRC Handbook of Chemistry and Physics*, edited by D. R. Lide (CRC, Boca Raton, FL, 1994).

[4] J. W. Raymonda, J. S. Muenter, and W. A. Klemperer, J. Chem. Phys. **52**, 3458 (1970).

[5] J. Raymonda and W. Klemperer, J. Chem. Phys. **55**, 232 (1971).

[6] G. L. Gutsev and L. Adamowicz, J. Phys. Chem. **99**, 13 412 (1995).

[7] C. Desfrançois, H. Abdoul-Carime, and J. P. Schermann, Int. J. Mod. Phys. B **10**, 1339 (1996).

[8] C. J. Reid, Int. J. Mass Spectrom. Ion Processes **124**, R25 (1993).

[9] C. J. Reid, Chem. Phys. Lett. **229**, 279 (1994).

[10] T. Inone and S. Iwata, J. Mol. Struct. **243**, 147 (1991).

[11] A. I. Boldyrev, J. Simons, V. G. Zakrzewski, and W. von Niessen, J. Phys. Chem. **98**, 1427 (1994).

[12] G. L. Gutsev and R. J. Bartlett, Chem. Phys. Lett. **265**, 12 (1997).

[13] M. Urban, J. Noga, S. J. Cole, and R. J. Bartlett, J. Chem. Phys. **83**, 4041 (1985).

[14] R. J. Bartlett, J. D. Watts, S. A. Kucharski, and J. Noga, Chem. Phys. Lett. **165**, 513 (1990).

[15] P. O. Widmark, P. A. Malmqvist, and B. O. Roos, Theor. Chim. Acta **77**, 291 (1990).

[16] ACES II is a program product of the Quantum Theory Project, University of Florida, written by J. F. Stanton, J. Gauss, J. D. Watts, M. Nooijen, N. Oliphant, S. A. Perera, P. G. Szalay, W. J. Lauderdale, S. R. Gwaltney, S. Beck, A. Balkova, D. E. Bernholdt, K.-K. Baeck, P. Rozyczko, H. Sekino, C. Huber, and R. J. Bartlett. Integral packages included are VMOL (by J. Almlöf and P. R. Taylor), VPROPS (by P. R. Taylor), and ABACUS (by H. J. Helgaker, Aa. Jensen, P. Jørgensen, and P. R. Taylor).

[17] G. L. Gutsev and R. J. Bartlett, J. Chem. Phys. **105**, 8785 (1996).

[18] G. L. Gutsev, M. Nooijen, and R. J. Bartlett, Chem. Phys. Lett. **276**, 13 (1997).

[19] M. Gutowski, P. Skurski, A. I. Boldyrev, J. Simons, and K. D. Jordan, Phys. Rev. A **54**, 1906 (1196).

[20] G. L. Gutsev, M. Nooijen, and R. J. Bartlett, Phys. Rev. A **57**, 1646 (1998).

[21] M. Gutowski, K. D. Jordan, and P. Skurski, J. Phys. Chem. **102**, 2624 (1998).

[22] H. Sekino and R. J. Bartlett, Int. J. Quantum Chem., Symp. **18**, 255 (1994).

[23] M. Nooijen and R. J. Bartlett, J. Chem. Phys. **102**, 3629 (1995).

[24] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

[25] K. D. Jordan and W. Luken, J. Chem. Phys. **64**, 2760 (1976).

[26] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **14**, 731 (1985).

[27] S. R. Langhoff and C. W. Bauschlicher, Chem. Phys. Lett. **211**, 305 (1993).