Vertical Ionization Energies of Naphthalene

O. Dolgounitcheva, V. G. Zakrzewski, and J. V. Ortiz*

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506-3701

Received: June 21, 2000; In Final Form: September 6, 2000

Electron propagator calculations provide an accurate assignment of the six lowest vertical ionization energies (IEs) of naphthalene. The first four states have π holes and the next two have σ holes. Two subsequent final states with σ-hole and π-hole character are close in energy. Significant shake-up character occurs in the fourth state and in the fifth π-hole state. Computational schemes based on low-order, perturbative improvements to Koopmans's theorem results are unlikely to be valid for these two states. Assignment of the seventh and eighth states is difficult, therefore. Higher IEs are in close agreement with features seen in photoelectron spectra and in Penning ionization electron spectroscopy.

Introduction

Penning ionization electron spectroscopy[1] yields information that may complement photoelectron spectra and thereby facilitate assignment of final states. Penning ionization occurs when a molecule, M, collides with a metastable atom, A*, such that

$$\mathrm{A}^* + \mathrm{M} \rightarrow \mathrm{A} + \mathrm{M}^+ + \mathrm{e}^- \qquad (1)$$

where the excitation energy of A exceeds the ionization energy (IE) of M. Penning ionization electron spectra (PIES) are given by the kinetic energy distribution of the ejected electron. The dependence of an ionization cross section on collision energy is sensitive to the diffuse portions of Dyson orbitals corresponding to the IEs of M. These orbitals, which may be considered overlaps between initial, N-electron states and final states with $N - 1$ electrons, are defined by

$$\psi^{\mathrm{Dyson}}(x_1) = \int \Psi_N(x_1,x_2,x_3,...,x_N)\Psi^*_{N-1}(x_2,x_3,x_4,...,x_N)\mathrm{d}x_2\mathrm{d}x_3\mathrm{d}x_4...\mathrm{d}x_N \qquad (2)$$

Recent PIES experiments[2,3] have shown that cationic states of naphthalene with π holes correspond to higher intensities than their σ-hole counterparts. Comparison of PIES and photoelectron spectra (PES)[4] enabled assignment of five cationic states with π holes. Numerous states with σ holes were assigned as well. These determinations were aided by electron propagator calculations[5] in the outer valence Green's function approximation (OVGF).[6]

The latter method and the partial third-order approximation (P3)[7] may be employed for the assignment of the lowest IEs of closed-shell, organic molecules.[8,9] For the perturbative arguments underlying P3 and OVGF to be valid, pole strengths (p), must be close to unity, where

$$p = \int |\psi^{\mathrm{Dyson}}(x_1)|^2 \mathrm{d}x_1 \qquad (3)$$

When OVGF and P3 calculations produce pole strengths that are below 0.8, there is a clear need for renormalized electron propagator methods such as the two-particle, one-hole Tamm−Dancoff approximation (2ph-TDA) and the third-order, algebraic, diagrammatic construction, or ADC(3).[6] Both methods have been useful in identifying shake-up states that are not assignable to single-hole, one-determinant wave functions. 2ph-TDA and ADC(3) retain a first-order treatment of states with two-hole, one-particle character.

A recent extension of the P3 approximation, the renormalized, nondiagonal, second-order (NR2) self-energy, retains these advantages of the 2ph-TDA and ADC(3) methods for IEs of closed-shell molecules.[10] In addition, the errors in NR2 IEs decrease as basis sets are improved. For a representative set of closed-shell molecules, average absolute errors for IEs below 20 eV were 0.49, 0.27, 0.22, and 0.17 eV for the cc-pVDZ, aug-cc-pVDZ, cc-pVTZ, and aug-cc-pVTZ basis sets,[11] respectively. NR2 calculations are especially advantageous for unsaturated hydrocarbons. For ethylene, NR2 IEs systematically approach experimental IEs and produce errors of approximately 0.1 eV for cc-pV5Z basis sets.[12] NR2 calculations also are more efficient with respect to arithmetic operations and do not require transformed two-electron repulsion integrals with four virtual indices. NR2 avoids evaluation of constant self-energy diagrams with divergent behavior in the limit of large numbers of electrons.[13]

To extend the assignment based on OVGF calculations[2] to states that may have significant shake-up character and to confirm the assignments that have been made for the lowest states, we presently apply the NR2 method to the vertical IEs of naphthalene.

Methods

Geometry optimizations were performed with Gaussian 98[14] at the HF/6-311G** level.[15] A qualitative survey of IEs and pole strengths with the P3, ADC(3), and NR2 methods used the same basis set. NR2 calculations were subsequently performed with the cc-pVTZ basis.[11] Carbon 1s molecular orbitals are dropped from propagator summations; all other molecular orbitals are retained. Propagator calculations are executed with newly developed program links that communicate with Gaussian 98.[16] To locate many of the shake-up states, it was necessary to allow up to 65 iterations to be performed in the matrix diagonalization routines.

---

* Author to whom correspondence should be addressed. E-mail: ortiz@ksu.edu.

10.1021/jp002248g CCC: $19.00

TABLE 1: Survey of Ionization Energies (eV)

state	KT	P3	ADC(3)	NR2	PIES ref 2	OVGF[a] ref 2
^2A_u	7.94	8.12 (0.88)	8.04 (0.87)	7.99 (0.86)	8.00	7.93
$^2B_{3u}$	8.68	8.78 (0.88)	8.70 (0.87)	8.63 (0.86)	8.80	8.56
$^2B_{2g}$	10.45	10.02 (0.86)	10.06 (0.84)	9.82 (0.82)	9.99	9.83
			12.14 (0.02)	12.14 (0.02)		
$^2B_{1g}$	12.22	11.16 (0.82)	10.96 (0.10)	10.76 (0.56)	10.85	11.13
				11.05 (0.16)		
				14.03 (0.06)		
^2A_g	12.98	11.48 (0.89)	11.72 (0.89)	11.40 (0.87)	11.4	11.39
$^2B_{3g}$	13.28	11.82 (0.88)	11.92 (0.89)	11.60 (0.86)	11.7	11.56
$^2B_{2u}$	14.21	12.66 (0.87)	12.82 (0.87)	12.44 (0.85)	12.22	12.56
$^2B_{3u}$	14.53	12.85 (0.79)	12.40 (0.22)	12.10 (0.42)	12.41	12.89
			13.21 (0.44)			
			14.05 (0.02)	15.11 (0.04)		
			15.40 (0.08)	15.42 (0.07)		

[a] cc-pVDZ basis.[11]

TABLE 2: NR2 cc-pVTZ Ionization Energies (eV)

state	KT	NR2	PIES ref 2
^2A_u	7.95	8.17 (0.86)	8.00
$^2B_{3u}$	8.69	8.82 (0.85)	8.80
$^2B_{2g}$	10.46	9.98 (0.81)	9.99
		12.11 (0.02)	
$^2B_{1g}$	12.24	10.86 (0.38)	10.85
		11.09 (0.33)	
^2A_g	12.95	11.51 (0.86)	11.4
$^2B_{3g}$	13.25	11.73 (0.86)	11.7
$^2B_{2u}$	14.18	12.55 (0.84)	12.22
$^2B_{3u}$	14.54	12.18 (0.35)	12.41
		13.04 (0.29)	
$^2B_{1u}$	15.38	13.56 (0.82)	13.32
$^2B_{2u}$	15.90	13.88 (0.83)	13.6
$^2B_{3g}$	15.86	13.96 (0.82)	14.0
^2A_g	16.64	14.49 (0.80)	14.4
$^2B_{1u}$	16.92	14.80 (0.76)	14.8
		15.36 (0.03)	
^2A_g	18.44	16.04 (0.77)	15.85
$^2B_{3g}$	19.17	16.49 (0.72)	16.3
$^2B_{2u}$	19.05	16.44 (0.40)	16.8
		16.61 (0.28)	

Results and Discussion

Survey of Methods. A survey of the lowest IEs obtained with various methods is undertaken for diagnostic purposes. Results obtained with the 6-311G** basis are displayed in Table 1 with experimental data and OVGF calculations from ref 2. Pole strengths corresponding to Koopmans's theorem (KT) results are not listed, for they are identically equal to unity.

Three final states with π holes are assigned consistently by all methods. For the lowest IE, where the final state has a ^2A_u label, perturbative corrections to KT results in the P3, ADC(3), and NR2 columns are small. Pole strengths between 0.85 and 0.9 are typical for low-lying IEs of closed-shell molecules. All approximations are in close agreement with experiment. In the next, $^2B_{3u}$ state, errors in the IE predictions are somewhat greater, but pole strengths remain large. The third, $^2B_{2g}$ state exhibits larger discrepancies between KT and the correlated approximations, but agreement with experiment is satisfactory. The P3 pole strength remains in this method's acceptable range. For the first time, a shake-up state of the same symmetry type with a small pole strength appears at a higher energy, 12.14 eV.

In the assignment of ref 2, the fourth state has a π hole and the label $^2B_{1g}$. P3 calculations are in agreement and yield a slightly smaller pole strength. Corrections to KT results are larger and the discrepancy with experiment is approximately 0.3 eV. ADC(3) calculations do not converge readily to a state with a large pole strength. Current algorithms succeeded in finding only a state at 10.96 eV with a pole strength of 0.1. This result provides a clear warning about the validity of the P3 calculation. NR2 calculations encounter three IEs, with the lowest corresponding to the largest pole strength. This value, 10.76 eV, is in closer agreement with the experimental value.

Three final states with σ holes, ^2A_g, $^2B_{3g}$, and $^2B_{2u}$, are assigned to states 5−7 in ref 2. P3 calculations again are in agreement. Corrections to KT results are large, but pole strengths remain acceptable for applications of P3. In the third case, the discrepancy with experiment is 0.44 eV. These discrepancies are somewhat worse for ADC(3), but NR2 results are within 0.22 eV of experiment in all three cases.

Consideration of the last π-hole state, $^2B_{3u}$, produces two warning signs for P3 (and for that matter, OVGF) calculations. The P3 IE differs from experiment by 0.44 eV and the pole strength is below 0.80. ADC(3) and NR2 calculations produce IEs with low pole strengths that are both above and below the IE for the σ-hole, $^2B_{2u}$ state. The NR2 state at 12.10 eV is close to the NR2 shake-up prediction at 12.14 eV discussed above that also pertained to a π-hole state, albeit with $^2B_{2g}$ symmetry.

These results indicate that the fourth and fifth π-hole states assigned in ref 2 should be examined with a renormalized electron propagator method and an improved basis set. It is likely that methods such as OVGF and P3 will not suffice for many higher IEs.

NR2 Ionization Energies. The superior efficiency of NR2 enables study of the IEs of naphthalene with the cc-pVTZ basis. Table 2 shows these results.

For the first three states with π holes, accurate IE predictions obtain. NR2 predictions increase by approximately 0.2 eV with the use of the larger basis set. The pole strength for the third state is somewhat lower than the other two. This result is accompanied by prediction of a shake-up $^2B_{2g}$ state at 12.11 eV.

For the $^2B_{1g}$ case, two states of approximately equal pole strength are predicted. The first coincides, somewhat fortuitously, with the PIES feature at 10.85 eV. Another state is found at 11.09 eV and may correspond to shoulders seen in PIES and PES. The Koopmans picture of these cationic states is inappropriate; shake-up character is dominant.

For the fifth and sixth states, there is close agreement between NR2 predictions and experiment. These IEs correspond clearly to the region of PIES intensity that is reduced with respect to PES.

In the σ-hole, $^2B_{2u}$ case, satisfactory agreement with experiment is elusive. The larger basis leads to an NR2 prediction of 12.55 eV and an increased discrepancy with the assigned value of 12.22 eV. Despite the consistency of these results and the large pole strength, it may be necessary to apply more advanced methods to this state.

The NR2 pole strength for the π-hole, $^2B_{3u}$ state at 12.18 eV indicates large shake-up character. This value is close to the $^2B_{2g}$ shake-up predicted at 12.11 eV. Another $^2B_{3u}$ state is predicted at 13.04 eV.

These values appear to contradict the order of the PIES assignment for the seventh and eighth states: σ-hole and π-hole, respectively. In NR2 calculations, the π-hole states are predicted at 12.11 and 12.18 eV and the σ-hole state is predicted at 12.55 eV. P3 and OVGF results, as they are based on more drastic approximations regarding shake-up character in final states, cannot be regarded as definitive for making these assignments.

IE predictions at higher energies appear to be in close agreement with values given in ref 2. There are no Koopmans-like final states with pole strengths above 0.85, but there are several marginal cases with values between 0.80 and 0.85. Experimental features at 16.3 and 16.8 eV have been assigned to $^2B_{3g}$ and $^2B_{2u}$ states, respectively, but the results of Table 2 suggest that there are three states in this energy range.

It is likely that more thorough searches for NR2 IEs will produce additional states below 17 eV that are not listed in Table 2. These results provide a qualitative description of the broad, overlapping features seen between 15.5 and 17 eV.

Conclusions

NR2 calculations give accurate vertical IEs for final states that may be qualitatively described at the KT level, where the pole strengths are close to unity. An assignment of the first six cationic states based on ab initio, electron propagator calculations is consistent with previous reports.[2] Significant shake-up character is manifested in a low pole strength for the fourth state, which has a π hole and a $^2B_{1g}$ label. For the fifth π-hole state, shake-up character is dominant. It is not clear whether this state precedes the third σ-hole state, which has a $^2B_{2u}$ label. Many higher IEs have been calculated and these results are in close agreement with PIES assignments.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-9873897, by the Petroleum Research Fund and by Gaussian, Incorporated.

References and Notes

(1) Niehaus, A. *Adv. Chem. Phys.* **1981**, *45*, 399.

(2) Yamauchi, M.; Yamakita, Y.; Yamakado, H.; Ohno, K. *J. Electron Spectrosc. Relat. Phenom.* **1998**, *88−91*, 155.

(3) Munakata, T.; Ohno, K.; Harada, Y.; Kuchitsu, K. *Chem. Phys. Lett.* **1981**, *83*, 243.

(4) Schmidt, W. *J. Chem. Phys.* **1977**, *66*, 828, and references therein.

(5) Ortiz, J. V. *Adv. Quantum Chem.* **1999**, *35*, 33.

(6) Niessen, W. von; Schirmer, J.; Cederbaum, L. S. *Comput. Phys. Rep.* **1984**, *1*, 57.

(7) Ortiz, J. V. *J. Chem. Phys.* **1996**, *104*, 7599.

(8) Ortiz, J. V. In *Computational Chemistry: Reviews of Current Trends*; Leszczynski, J., Ed.; World Scientific: Singapore, 1997; Vol. 2, p 1.

(9) Ortiz, J. V.; Zakrzewski, V. G.; Dolgounitcheva, O. In *Conceptual Trends in Quantum Chemistry*; Kryachko, E. S., Ed.; Kluwer: Dordrecht, 1997; Vol. 3, p 465.

(10) Ortiz, J. V. *J. Chem. Phys.* **1998**, *108*, 1008.

(11) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007; Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *ibid* **1992**, *96*, 6796.

(12) Dolgounitcheva, O.; Zakrzewski, V. G.; Ortiz, J. V. *J. Chem. Phys.*, accepted for publication.

(13) Deleuze, M.; Delhalle, J.; Pickup, B. T.; Calais, J.-L. *Adv. Quantum Chem.* **1995**, *26*, 35.

(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Peterson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al- Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98*, Revision A8; Gaussian, Inc.: Pittsburgh, PA, 1998.

(15) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(16) Zakrzewski, V. G.; Dolgounitcheva, O.; Ortiz, J. V. *Int. J. Quantum Chem.* **1999**, *75*, 607.