

THEORETICAL STUDIES OF MOLECULAR IONS. VERTICAL DETACHMENT ENERGY OF OH⁻

Wesley D. SMITH, Tsung-Tai CHEN and Jack SIMONS *

*Chemistry Department, University of Utah,
Salt Lake City, Utah 84112, USA*

Received 26 April 1974

The $1\Sigma^+ \rightarrow 2\Pi_1$ vertical electron detachment energy of OH⁻ is studied using a basis of twenty Slater-type orbitals in our equations-of-motion (EOM) theory of molecular electron affinities and ionization potentials. The delicate balance between the contributions of orbital reorganization effects and correlation energy change to the calculated negative-ion detachment energy is demonstrated clearly. Comparisons are made with the results of very precise experimental photodetachment measurements and with other theoretical predictions.

1. Introduction

The energetics of the gas-phase detachment of an electron from the hydroxide anion was first probed in a thorough manner by Smith and Branscomb [1] in 1955. More recently Branscomb [2], Hotop et al. [3], and Celotta et al. [4] used laser light sources and higher resolution instruments to determine the detachment threshold to a greater degree of precision. The results of these excellent experimental studies allow us to conclude that the bond lengths R_e and vibrational frequencies ω_e of OH and OH⁻ are very nearly the same and that the detachment energy of OH⁻ is 1.825 ± 0.002 eV. Because $|\omega_e(\text{OH}) - \omega_e(\text{OH}^-)| \leq 0.016$ eV and $|R_e(\text{OH}) - R_e(\text{OH}^-)| \leq 0.001$ au, the experimental detachment results, which measure $E(\text{OH}, 2\Pi_1, \nu=0) - E(\text{OH}^-, 1\Sigma^+, \nu=0)$ should agree to within 0.02 eV with either the vertical electron detachment energy of OH⁻ or the vertical electron affinity of OH. Thus, the comparison of our calculated vertical electronic energy difference with the experimentally determined $\nu=0 \rightarrow \nu=0$ threshold is entirely appropriate for this specific negative molecular ion.

The pioneering theoretical work on the electron affinity of OH was carried out by Cade [5] in 1967. In

his very important work on negative molecular ions, extended-basis Hartree-Fock calculations were performed on both OH and OH⁻ at many internuclear distances. Cade then used the known change in correlation energy ΔE_{corr} , which accompanies ionization of the isoelectronic Ne atom, together with an approximate correction for the nuclear-charge dependence of ΔE_{corr} , to obtain his prediction of 1.91 eV for the electron affinity of OH. In performing these calculations, Cade found that the Koopmans' theorem [6] detachment energy of OH⁻ was 2.90 eV for his basis, while the difference in the SCF energies of OH and OH⁻ at $R = 1.795$ au predicted an electron affinity of -0.10 eV for OH. These results show clearly that both orbital relaxation and correlation energy change which accompany removal of an electron play very important roles in determining the detachment energy of OH⁻. It follows that any calculation whose aim is the prediction of an ion-molecule energy difference must treat these two competing effects properly and on equal footing.

In section 2 of this paper, we briefly discuss a direct-calculation approach which satisfies the above requirement and which we have employed [7,8] in our studies of the ionization potentials of HF and N₂ as well as the present investigation of the vertical electron detachment energy of OH⁻. Section 3 contains an

* Alfred P. Sloan Foundation Fellow.

analysis of our results, a comparison with experimental and other theoretical predictions, and our concluding remarks.

2. The equations-of-motion theory

In an earlier publication [9], we succeeded in developing a quantum chemical method which permits us to calculate ion-molecule energy differences directly, rather than as a result of two separate variational calculations on the molecule and the ion. In our theory, factors which, through third order in the electron interactions r_{ij}^{-1} , contribute equally to the energies of the ion and molecule are formally cancelled. Only the energy difference, which is accurate through third order [10], is actually calculated.

Moreover, we have demonstrated [7,8] that our technique can be used to separately assess the contributions of orbital reorganization and correlation energy change to the calculated ionization energy. In carrying out such analyses on HF and N₂, we found that the effects due to orbital relaxation are most important for ionizations of these neutral species. However, if one is interested in obtaining ionization potentials which are accurate to within 1 eV, both the correlation energy change which accompanies ionization and the orbital reorganization effects must be handled properly. This conclusion bears even more heavily on the research which is presented in this paper, because an error of 1 eV is intolerable when one is studying the detachment energy of a negative ion; the detachment energy itself is of the order of one or two eV's or less.

In our EOM approach, the electron affinity or ionization potential ($-\Delta E$) of a closed-shell species* is obtained by solving a matrix pseudo-eigenvalue problem.

$$\mathbf{H}(\Delta E)\mathbf{X} = \Delta E\mathbf{X}, \quad (1)$$

where the elements of the $\mathbf{H}(\Delta E)$ matrix are given in terms of the Hartree-Fock orbital energies and two-

electron integrals of the parent in eqs. (31)–(37) of ref. [9]. For the sake of brevity, these equations will not be reproduced here. In the calculations reported here, the $\text{OH}^- \text{X } ^1\Sigma^+$ ion is identified as the closed-shell parent and the vertical detachment energy is computed as the lowest ionization potential of this parent. The other pseudo-eigenvalues of $\mathbf{H}(\Delta E)$ correspond to higher ionization potentials in which the daughter OH is excited [9]. In this paper, our discussion is limited to the vertical detachment of an electron from $\text{X } ^1\Sigma^+ \text{OH}^-$ to the $^2\Pi_i$ state of OH.

In solving eq. (1) using the iterative procedure described in refs. [7–9], the fact that $\mathbf{H}(\Delta E)$ is block diagonalized according to molecular symmetry reduces the problem to one of finding a specific pseudo-eigenvalue of the π -block of $\mathbf{H}(\Delta E)$. Beginning the iterative process with ΔE approximated by the orbital energy of the occupied π -orbital of OH^- (Koopmans' theorem) allows us to converge to the desired $^2\Pi_i$ ionization energy. The methods which are used to accelerate the convergence of the iterative procedure are discussed in refs. [7–9].

As was shown in ref. [9] and subsequently applied to studies of the ionization potentials [7,8] of HF and N₂, the matrix $\mathbf{H}(\Delta E)$ appearing in our EOM theory can be decomposed into two components each of which has a specific physical meaning:

$$\mathbf{H}(\Delta E) = \mathbf{H}^{(1)} + \mathbf{H}^{(2)}. \quad (2)$$

$\mathbf{H}^{(1)}$ contains the Koopmans' theorem estimate of the ionization energy and the contributions which are made by orbital relaxation or charge redistribution effects. The second component $\mathbf{H}^{(2)}$ treats the change in electron correlation energy which accompanies either removal or addition of an electron to the parent species. Of course, this decomposition of $\mathbf{H}(\Delta E)$ does not rigorously imply that the calculated detachment energy ($-\Delta E$) is a sum of two terms each due to one of the physical effects described above. However, a comparison of the SCF results of other investigators** with our EOM results on the ionization potentials of HF and N₂ in which $\mathbf{H}^{(2)}$ is excluded gives evidence that the effects of mixing or interference between $\mathbf{H}^{(1)}$ and $\mathbf{H}^{(2)}$ on the computed ΔE are small. Thus, it is our feeling that the value of ΔE which is obtained

* At present our theory is restricted to studying ion-neutral energy differences in which either the ion or the neutral is closed-shell. We are currently in the process of extending our method to permit the study of systems in which both the ion and neutral are open-shell.

** See refs. [7,8] for a detailed discussion of these comparisons.

by finding the appropriate pseudo-eigenvalue of $H^{(1)}(\Delta E)$ represents a valid EOM approximation to the parent-daughter SCF energy difference. In table 2, we present such approximate SCF detachment energies for the OH^- ion being studied in the present work.

3. Results and discussion

In carrying out the EOM calculations described here, we employed two atomic orbital bases consisting of Slater-type functions whose orbital exponents were taken from the bases of Cade [5] for OH^- and of Cade and Huo [11] for OH. Information describing one of our bases and the essential results of the SCF calculation on the parent $X^1\Sigma^+ OH^-$ for this basis is given in table 1. Another basis of twenty orbitals which is formed by replacing the two O $3d_\pi$ functions by two O 1s functions with orbital exponents equal to 12.3850 and 2.3507 has also been used here and will be referred to as basis (O $3d_\pi \rightarrow 1s$). The SCF energy for basis (O $3d_\pi \rightarrow 1s$) is -75.3871 au which is a very substantial

improvement over the SCF energy reported in table 1. Clearly, this large difference in SCF energies is due to the fact that the lowest energy orbital of OH^- , which is largely O 1s in character, is described more accurately in basis (O $3d_\pi \rightarrow 1s$) than in the basis of table 1. That is, basis (O $3d_\pi \rightarrow 1s$) gives an improved description of the core electrons of OH^- whereas the basis which contains the O $3d_\pi$ polarization functions gives a better description of the π valence electrons.

To clarify our reasons for working with the basis given in table 1, which admittedly gives a rather poor description of the lowest molecular orbital of OH^- , let us now turn to a discussion of the computed electron detachment energies which result from our third-order EOM calculations. As shown in table 2, the vertical detachment energies computed using the basis of table 1 and the basis (O $3d_\pi \rightarrow 1s$) differ by only 0.02 eV and are within 0.10 eV of the experimental result quoted by Lineberger et al. [3]. The important observation which should be made here is that the basis given in table 1, which yields a poor SCF energy for the reasons explained above, is capable of yielding a very accurate detachment energy. The improved de-

Table 1

20-function Hartree-Fock wavefunction for OH^- . $R = 1.781$ au, $E = -75.0060$ au, $\epsilon_{1\sigma} = -20.1677$, $\epsilon_{2\sigma} = -0.9028$, $\epsilon_{3\sigma} = -0.2044$, $\epsilon_{1\pi} = -0.1124$

| σ atomic orbitals | 1σ | 2σ | 3σ | π atomic orbitals | 1π |
|--------------------------|-----------|-----------|-----------|-----------------------|--------|
| O 1s (7.0168) | 1.0250 | -0.2549 | 0.0713 | O 2p (0.9504) | 0.3295 |
| O 2s (1.5729) | 0.0943 | 0.4841 | -0.3726 | O 2p (2.0624) | 0.4041 |
| O 2p (1.0227) | 0.3224 | 0.0281 | 0.0751 | O 2p (3.7529) | 0.2527 |
| H 1s (1.1986) | -0.1220 | -0.0840 | 0.5996 | O 2p (1.2659) | 0.1354 |
| O 2s (2.8646) | -0.0958 | 0.5415 | -0.1611 | O 3d (1.6635) | 0.0311 |
| O 2p (2.1172) | -0.0099 | 0.1038 | 0.6252 | H 2p (1.7699) | 0.0321 |
| H 1s (2.4385) | 0.0294 | 0.1082 | -0.0320 | | |
| H 2p (2.3003) | 0.0577 | 0.1141 | -0.0489 | | |

Table 2

Summary of the electron detachment energy calculations on $X^1\Sigma^+ OH^- \rightarrow e^- + X^2\Pi_i OH$ (energies in eV)

| Basis used | Koopmans' theorem | $-\Delta E_{SCF}^a$ | ν_i EOM ^{b)} | Experiment [3] |
|------------------------------------|-------------------|---------------------|---------------------------|-------------------|
| basis of table 1 | 3.06 | -0.20 | 1.76 | 1.825 \pm 0.002 |
| basis (O $3d_\pi \rightarrow 1s$) | 3.05 | -0.15 | 1.74 | |

a) Our approximation to the ion-neutral SCF energy difference obtained by neglecting the correlation contribution to $H(\Delta E)$.

b) On a Univac 1108 computer, the SCF procedure and two-electron integral transformation required 5 minutes; the EOM detachment energy calculation required 3 minutes.

scription of the core electrons which is achieved by using basis ($O3d_{\pi} \rightarrow 1s$) is not needed for the detachment energy calculation. In fact, the presence of the $O3d_{\pi}$ orbitals, which improve the description of the valence electron space, yields a slightly better detachment energy. We have made analogous observations [7,8] in the course of our studies of the vertical ionization potentials of HF and N_2 , as have Sasaki and Yoshimine [12] in their investigations of the electron affinities of B, C, N, O, and F. We are thus led to conclude that, even for first-row atoms, an accurate description of the core orbitals is not essential if one is interested in computing valence-shell ionization energies.

To assess the contributions of orbital relaxation and correlation energy change to the computed detachment energy of OH^- , we refer to the results labeled ΔE_{SCF} in table 2. These results constitute our approximation, for the two bases employed, to the ion-neutral Hartree-Fock energy difference. They were obtained, as described earlier, by deleting the correlation contributions ($H^{(2)}$) to the matrix $H(\Delta E)$ in our iterative solution of eq. (1). The fact that such Hartree-Fock level calculations predict a negative detachment energy for OH^- , which is in agreement with Cade's earlier observation [5], implies that the ion-molecule correlation energy difference must be properly treated if one is to have any hope of understanding the stability of negative ions. Because the detachment energies of negative ions are commonly of the same magnitude as the ion-neutral correlation energy differences, the neglect or improper treatment of correlation effects is intolerable.

In conclusion, we have shown that the EOM theory of molecular electron affinities and ionization potentials developed in ref. [9] is capable of yielding the vertical electron detachment energy of $X^1\Sigma^+ OH^-$ to within 0.1 eV. We have also demonstrated that a highly accurate description of the core orbital of OH^- is not essential to an accurate calculation of the $^2\Pi_1$ valence electron detachment energy. Finally, an investi-

gation of the roles of orbital relaxation and correlation energy change in determining the ion-molecule energy difference has led to the conclusion that both of these effects must be treated properly in any study of negative molecular ions.

At present we are not only extending our EOM investigations of the detachment energies of chemically interesting negative ions but we are also using our EOM method to calculate photoionization cross sections of neutral molecules, detachment cross sections of negative ions, and the first-order reduced density matrices of closed-shell species [13]. Results of these studies should be appearing shortly.

Acknowledgement

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References

- [1] S.J. Smith and L.M. Branscomb, *Phys. Rev.* 99 A (1955) 1657.
- [2] L.M. Branscomb, *Phys. Rev.* 148 (1966) 11.
- [3] H. Hotop, T.A. Patterson and W.C. Lineberger, *J. Chem. Phys.* 60 (1974) 1806.
- [4] R.J. Celotta, R.A. Bennett and J.L. Hall, *J. Chem. Phys.* 60 (1974) 1740.
- [5] P.E. Cade, *J. Chem. Phys.* 47 (1967) 2390.
- [6] T. Koopmans, *Physica* 1 (1934) 104.
- [7] T.-T. Chen, W.D. Smith and J. Simons, *J. Chem. Phys.*, to be published.
- [8] T.-T. Chen, W.D. Smith and J. Simons, *Chem. Phys. Letters* 26 (1974) 296.
- [9] J. Simons and W.D. Smith, *J. Chem. Phys.* 58 (1973) 4899.
- [10] J. Simons, *Chem. Phys. Letters* 25 (1974) 122.
- [11] P.E. Cade and W.M. Huo, *J. Chem. Phys.* 47 (1967) 614.
- [12] F. Sasaki and M. Yoshimine, *Phys. Rev.* A9 (1974) 26.
- [13] J. Simons, *J. Chem. Phys.* 59 (1973) 2436.