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Isotope shift in the oxygen electron affinity

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The present paper reports the *ab initio* evaluation of the electron affinity of oxygen, and the value of its isotope shift. The theoretical results are in good agreement with the recent electron affinity measurements for ^{16}O and^{18}O by photodetachment microscopy, revealing an ''anomalous'' isotope shift. The theoretical fine structure of the negative ion $2p^5\ ^2P^o_{1/2-3/2}$ is also in very good agreement with observation.
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Introduction. Electron correlation plays a crucial role in both the stability of negative ions and in the specific mass shift property. Experimentally, the electron affinities of atomic hydrogen and deuterium have been determined by tunable-laser threshold-photodetachment spectroscopy [1], confirming the predicted shift in theory [2]. Isotope shifts of the H$^-$($^1P^o$) dipole resonances below the H($n=2$) threshold have also been determined for both H$^-$ and D$^-$ by Doppler-tuned collinear laser spectroscopy [3], allowing a critical test for predicted isotope effects [4]. The measured hydrogen-deuterium isotope shift in the energy of the lowest ^1D autodetaching resonance in H$^-$ and D$^-$ by Rislove *et al.* [5] conflicted with the theoretical predictions. Hopefully, the source of this disagreement has been found recently in a sign error made when extracting the mass polarization contribution from the measured isotope shift [6]. So, theory preceded observation for these H/H$^-$ and D/D$^-$ pairs. The isotope shift in the electron affinity between ^{35}Cl and ^{37}Cl has been measured by tunable-laser photodetachment spectroscopy [7]. The many-body calculations presented in the same work [7], combined with the experimental accuracy achieved, demonstrated that the inclusion of higher-order correlation effects would be necessary for a quantitative description. In view of the extreme difficulty of the theoretical treatment of isotope shifts in Cl and Cl$^-$, a suggestion made by Berzinsh *et al.* [7] was to investigate few-electron systems, such as Li$^-$, for which more accurate calculations could be feasible. Unfortunately, the experimental conditions are unfavorable for this system.

Progress has been achieved recently through the ^{16}O and ^{18}O electron affinity measurements of Valli *et al.* [8], using photodetachment microscopy [9]. The multiconfiguration Hartree-Fock (MCHF) procedure has been successfully used for evaluating the electron affinity of lithium [10], boron [11], and calcium [12]. Line or transition isotope shifts have been calculated using variational MCHF wave functions in light systems [13,14]. In the present work, we report calculations of not only the oxygen electron affinity, but also the isotope shift in this property.

The electron affinity. Systematic calculations of MCHF wave functions and total energies were performed with orbital active sets (AS's) of increasing size. A good description of the neutral atom could be obtained through an expansion over configuration states obtained by single (S) and double (D) excitations from the $1s^22s^22p^4$ reference configuration. But this process ignores the near degeneracy of the $2s$ and $2p$ orbital energies, so we allow $2s-2p$ replacements in addition to *SD* excitations to unoccupied orbitals. At the same time, since the correlation with $1s^2$ will largely cancel, we restrict the $1s$ orbital to being at least singly occupied. The resulting expansion is over the set of possible configuration states described in a ''layer'' notation by $1s\{1,2\}^5\{2,3,\ldots,n\}^2$. In other words, every configuration state in the MCHF expansion contains at least one $1s$ electron; the next five electrons are either $1s$, $2s$, or $2p$, whereas the remaining two electrons are unrestricted, except by the resultant angular momentum and parity. All possible angular-momentum couplings are considered. In the negative ion, an electron is added to a ''core.'' Two factors need to be considered. The $2s^22p^5$ label for the ground state of O$^-$ suggests the addition of an equivalent electron, but a much better wave function is obtained by allowing this orbital to be nonequivalent, which, in an orthogonal approach, leads to an expansion over $2s^22p^5$ and $2s^22p^43p$. At the same time, as in photodetachment calculations [15], it is necessary to recognize the possibility of cores of different parity and different outer orbitals. An example in this case would be the configuration state $2s2p^53s$. A possible multireference set for *SD* excitations, in our layer notation, would be $1s^2\{2\}^6\{2,3\}$. But again, these *SD* excitations do not take into account the near degeneracy effects between $2s$ and $2p$, and so we used expansions over the set as indicated in Table I. In all the expansions, the higher angular momenta correspond to $l_{max}=4$, i.e., g orbitals. All the orbitals are variational, except the $1s$ orbital, which is kept frozen from the $n=3$ calculation of O$^-2p^5\ ^2P^o$.

The number of configuration state functions (NCSF's), total energies for O$^-$ and O, together with the corresponding

TABLE I. Models for generating the multiconfiguration expansions.

AS	O$^-2p^5\ ^2P^o$	O $2p^4\ ^3P$
$n=3$	$1s\{1,2\}^5\{2,3\}^3$	$1s\{1,2\}^5\{2,3\}^2$
$n\geqslant4$	$1s\{1,2\}^5\{2,3\}\{2,3,\ldots,n\}^2$	$1s\{1,2\}^5\{2,3,\ldots,n\}^2$

TABLE II. Number of CSF's, total energies, and electron affinities for the different active sets.

	$O^- 2p^5\ ^2P^o$		$O\, 2p^4\ ^3P$		
AS	NCSF	E (a.u.)	NCSF	E (a.u.)	E_a (eV)
HF	1	-74.7897459	1	-74.8093984	-0.5349
$n=3$	544	-74.9777484	150	-74.9475811	0.8209
$n=4$	5315	-75.0321448	724	-74.9893778	1.1637
$n=5$	18 345	-75.0557791	1934	-75.0054340	1.3700
$n=6g$	39 656	-75.0633109	3777	-75.0099715	1.4514
$n=7g$	69 248	-75.0660526	6253	-75.0116553	1.4802
	$O^- 2p^5\ ^2P^o_{3/2}$		$O\, 2p^4\ ^3P_2$		
$n=7gr$	69 248	-75.1157987	6253	-75.0617630	1.4704

electron affinity value (E_a), are reported in Table II for the different orbital active sets. In the one-configuration Hartree-Fock (HF) approximation, the electron affinity has the wrong sign. It stabilizes quickly when extending the orbital active set, with the convergence being close to two decimal places. The relativistic correction has been estimated by performing a Breit-Pauli calculation (omitting the orbit-orbit interaction) for both the negative ion and the neutral atom. The corresponding results are labeled ''$7gr$.'' The electron affinity is then the energy difference $E_a = E(O\, 2p^4\ ^3P_2) - E(O^- 2p^5\ ^2P^o_{3/2})$. The relativistic effect on the electron affinity is small (9.8 meV), but not negligible.

The theoretical fine-structure energy separations of $2p^4\ ^3P_{2,1,0}$ for neutral oxygen and of $2p^5\ ^2P^o_{3/2,1/2}$ for O^- are compared in Table III with observation [16,8]. The agreement is rather good.

The final electron affinity is compared with other theories and observation in Table IV. The electron affinity of oxygen has been evaluated *ab initio* using a systematic configuration-interaction (CI) approach [17], and single- and double-multireference CI expansions involving large basis sets [18,19]. More limited CI results are also reported in a work on photodetachment cross sections [20]. The coupled-cluster method, including all single, double, and perturbative triple excitations [CCSD(T)] [21], and the density functional theory [22] have also been attempted. The large dispersion of the theoretical results illustrates the difficulty in evaluating electron affinities. From the experimental point of view, the electron affinity has been measured by laser photodetachment spectroscopy (LPS) [23], but the value needed to be reevaluated, as described by Blondel [24]. It has also been determined by photodetachment microscopy (PM) [8] for both ^{16}O and ^{18}O isotopes.

TABLE III. Fine-structure splittings in $O^- 2p^5\ ^2P^o$ and $O\, 2p^4\ ^3P$.

	$O^- 2p^5\ ^2P^o$ E (cm^{-1})			$O\, 2p^4\ ^3P$ E (cm^{-1})	
J	This work	Observed [8]	J	This work	Observed [16]
3/2	0.0	0.0	2	0.0	0.0
1/2	178.33	177.085(27)	1	159.41	158.265
			0	230.07	226.977

TABLE IV. Electron affinity of oxygen ^{16}O (in eV): comparison of theory and observation.

E_a	Method and reference
	Theory
1.31–1.36	CI [17]
1.454	MRCI [18]
1.384	MRSD-CI [19]
1.415	CCSD(T) [21]
1.62	DFT hybrid method [22]
1.4	MRCI [20]
1.4704	MCHF+BP (this work)
	Experiment
1.461 110 7(17)	LPS [23,24]
1.461 1149(26)	PM [8]

The $^{18-16}(O^- - O)$ *isotope shift.* The new measurements by photodetachment microscopy [8] resolve the ^{16}O and ^{18}O isotopic thresholds. The difference between the two electron affinities $E_a(^{18}O) - E_a(^{16}O) = -0.070(27)$ cm^{-1} is negative, corresponding to a smaller energy for the heavier isotope. This isotope shift, converted to $-8.68\ 10^{-6}$ eV, is rather small relative to the detachment energy or electron affinity reported in Table IV, and negligible in comparison with the dispersion of the theoretical results. One can, however, try to estimate this shift using an *ab initio* approach.

The mass shift of an energy level, can be derived by treating the mass polarization term $(1/M)\Sigma_{i<j}\mathbf{p_i}\cdot\mathbf{p_j}$ as a small perturbation [25]. Keeping only the first-order specific mass shift (SMS) correction, the mass shift has the form [26,27]

$$E_M - E_\infty = -\frac{\mu}{M}E_\infty + \left(\frac{\mu}{m_e}\right)\frac{1}{(M+m_e)}\left\langle \psi_\infty \middle| \sum_{i<j}^{N} \mathbf{p_i}\cdot\mathbf{p_j} \middle| \psi_\infty \right\rangle. \tag{1}$$

where $\mu = m_e M/(m_e + M)$ is the reduced mass and E_∞ is the (negative) eigenvalue of the infinite nuclear mass problem. The first term is known as the normal mass shift (NMS). In atomic units (energy in $E_h = e^2/a_0$, masses expressed in m_e, linear momentum in $\hbar$), Eq. (1) can be rewritten as

$$E_M = \frac{M}{1+M}E_\infty + \frac{M}{(1+M)^2}S_{SMS}, \tag{2}$$

where

$$S_{SMS} \equiv -\left\langle \psi_\infty \middle| \sum_{i<j}^{N} \boldsymbol{\nabla}_i\cdot\boldsymbol{\nabla}_j \middle| \psi_\infty \right\rangle. \tag{3}$$

Considering the mass dependency of the total energy for both the negative ion and the neutral atom, the mass-dependent electron affinity has the form

$$E_a^M = E_M(O) - E_M(O^-)$$

$$= \frac{M}{1+M}E_a^\infty + \frac{M}{(1+M)^2}\Delta S_{SMS}, \tag{4}$$

TABLE V. Normal mass shift (NMS), specific mass shift (SMS), and total isotope shifts on the electron affinity.

	$O^- 2p^5\ ^2P^o$	$O\ 2p^4\ ^3P$	$^{18-16}$O isotope shifts (cm^{-1})		
AS	S_{SMS}	S_{SMS}	ΔE_a^{NMS}	ΔE_a^{SMS}	ΔE_a
HF(O^-)	−6.127 198 66	−4.901 758 93	0.080 81	−1.027 56	−0.946 75
HF	−6.127 198 66	−5.849 697 63	−0.016 48	−0.232 69	−0.249 17
5	−4.907 368 49	−4.767 392 78	0.042 22	−0.117 37	−0.075 15
6*g*	−4.889 231 04	−4.765 345 57	0.044 73	−0.103 88	−0.059 15
7*g*	−4.888 101 26	−4.766 061 14	0.045 62	−0.102 33	−0.056 72
7*g*[a]	−4.888 101 26	−4.766 061 14	0.045 03	−0.102 33	−0.057 30
Obs. [8]			0.045	−0.115(27)	−0.070(27)

[a] NMS calculated using the observed electron affinity.

where

$$\Delta S_{SMS}=S_{SMS}(\mathrm{O})-S_{SMS}(\mathrm{O}^-). \tag{5}$$

The isotope shift in the electron affinity is defined as the difference of the electron affinities between the two isotopes. According to Eq. (4), it has the form

$$\begin{aligned}\Delta E_a(^{18-16}\mathrm{O})&=E_a(^{18}\mathrm{O})-E_a(^{16}\mathrm{O})\\&=\Delta E_a^{NMS}(^{18-16}\mathrm{O})+\Delta E_a^{SMS}(^{18-16}\mathrm{O}),\end{aligned} \tag{6}$$

with

$$\Delta E_a^{NMS}(^{18-16}\mathrm{O})=\left[\frac{M_{18}}{(1+M_{18})}-\frac{M_{16}}{(1+M_{16})}\right]E_a^{\infty} \tag{7}$$

and

$$\Delta E_a^{SMS}(^{18-16}\mathrm{O})=\left[\frac{M_{18}}{(1+M_{18})^2}-\frac{M_{16}}{(1+M_{16})^2}\right]\Delta S_{SMS}, \tag{8}$$

where M_A is the mass of itosope A. Due to the positive sign of the mass factor ($M_{18}>M_{16}$) in Eq. (7), the normal mass shift contribution to the shift in the electron affinity has the same sign as the electron affinity itself (positive in the present case). The mass factor of Eq. (8) being negative, the specific mass shift contribution to the isotope shift in the electron affinity will counteract the NMS if $\Delta S_{SMS}\geqslant 0$.

The expectation values of the two-body operator, calculated S_{SMS} using the infinite nuclear mass MCHF eigenfunction Ψ_∞, are reported in Table V for both the negative ion and the neutral atom, and monitored as a function of the active set, together with the NMS (7) and SMS (8) contributions to the shift in the electron affinity. The mass factors for the (18–16) isotope pair of oxygen have been calculated using the atomic masses from the table of Audi and Wapstra [28].

As discussed above, a negative sign of the specific mass shift $\Delta E_a^{SMS}(^{18-16}\mathrm{O})$ results from a positive ΔS_{SMS} value. The sign of the latter can be easily understood from the analysis of the energy expression. For the angular integration, the $\boldsymbol{\nabla}_i\cdot\boldsymbol{\nabla}_j$ operator indeed behaves like the scalar product of the rank-one components $\mathbf{C}_i^{(1)}\cdot\mathbf{C}_j^{(1)}$ appearing in the expansion of the Coulomb electrostatic interaction $1/r_{ij}$. Therefore, a product of radial Vinti integrals $J(nl,n'l')J(n'l',nl)=-J^2(nl,n'l')$ appears at each occurrence of an exchange $G^1(nl,n'l)$ integral [29] in the total energy expression. In this respect, if the same orbital basis set is used for the negative ion and the neutral atom, the only difference between the eight- and nine-electron system is the $(2*n)$ pair-number weighing factor of the $G^1(1s,2p)$ and $G^1(2s,2p)$, where n is the occupation number of the subshell $2p^n$. The calculation of Eq. (5) then gives

$$\Delta S_{SMS}=-\tfrac{1}{6}(8-10)[J^2(1s2p)+J^2(2s2p)], \tag{9}$$

which must be a positive quantity, producing a negative ΔE_a^{SMS} contribution to the electron affinity isotope shift. This is indeed observed in the one-configuration Hartree-Fock calculation [labeled HF(O^-) in Table V], using the O^- orbital basis for both the negative ion and the neutral atom. When separately optimized HF wave functions are used, the Vinti integrals are no longer identical for the two systems and the factorization (9) does not apply anymore. The specific mass shift on the electron affinity decreases substantially, but the Hartree-Fock approximation is not adequate, even though it predicts the right sign of ΔE_a^{SMS}. As can be seen from Table V, the introduction of electron correlation is crucial. The $n=7g$ orbital active set gives a converged SMS result at the percent level of accuracy.

Experimentally, the specific mass shift is determined by substracting the NMS shift (which can be evaluated from the experimental electron affinity) from the difference of the electron affinities measured for the two isotopes [8]. As can be seen, the theoretical result lies within the error bars and the agreement is rather good. As suggested by the convergence of ΔE_a^{SMS}, the theoretical error is smaller than the experimental uncertainty.

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