Natural widths in open-shell atoms: The K absorption spectrum of atomic oxygen

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Total-ion-yield measurements and Hartree-Fock calculations are presented for the $1s \rightarrow np$, $n=2$ to 5 photoexcitations in atomic oxygen. Energies and relative intensities of the $[1s]2s^2 2p^4(^4P)np$ and $[1s]2s^2 2p^4(^2P)np$ series members are determined, and the apparent linewidths are measured. It is shown that natural widths in an open-shell atom can be deduced from an absorption spectrum only with the aid of theoretical input. The linewidth for the six individual components contained in the $1s \rightarrow 2p$ transition is determined to be 140(9) meV. [S1050-2947(96)50308-2]

The natural width of a level is due to the finite lifetime of the corresponding hole state and represents one of the basic properties of an atom. As such, many studies have been aimed at determining this property. However, for most elements, investigations have been limited, regardless of the method applied, to condensed or molecular systems in which the natural width of an atomic level is masked or influenced in a myriad of ways [1,2]. Chemical and solid-state effects such as multiplet splitting, crystal fields, vibrational structure, ligand fields, and valence electron densities place serious limitations, even for high-resolution studies [3–5], on the reliability of the values of this atomic property extracted from the data. The limitations are exacerbated in determinations that rely on measurements of linewidths, because most effects apply to each of the levels involved in the transition. Few restrictions obtain to the rare gases, although, even then, consideration must be given to isotope effects [6], interactions between the particles produced [7], the presence of an excited electron [8], and multiple, including secondary, ionization events [1,9,10], depending upon the particulars of the case at hand.

An experimental determination of the natural width in an open-shell atom has not been delineated so far, although some potentially suitable inner-shell studies have been reported [11–13]. We demonstrate by way of a high-resolution photoabsorption measurement that this task is much more complex than in a closed-shell configuration and, in the general case, cannot be accomplished without the assistance of theoretical input for proper definition of the width of a level or a transition. We support the analysis of the data by a calculation of energies and rates of transitions relevant to the excitation of a K electron in the oxygen atom chosen for this work.

In addition to providing a benchmark value for the transition and level widths of K-shell excited atomic oxygen, the present study provides the entire photoabsorption spectrum in this open-shell atom, yielding the energies and the relative intensities of the principally resolvable members of the two absorption series converging to the $[1s]2s^2 2p^4(^4P)$ and $[1s]2s^2 2p^4(^2P)$ ionization thresholds. Such data are not only of intrinsic value, presenting a challenge to theory, but are of importance for quantitative evaluation of upper atmospheric and interstellar processes [14,15] and for disentangling lifetime and chemical effects in molecular and solid-state systems.

The total-ion-yield experiment (equivalent to photoabsorption) was performed at the high-resolution HERMON monochromator [16] of the Wisconsin Synchrotron Radiation Center. Atomic oxygen was produced by dissociation of molecular oxygen in a microwave-driven discharge as described elsewhere [17]. The ions created by the incoming radiation were extracted in a strong field, accelerated to 3 keV, and detected by means of a channeltron which was mounted perpendicular to the photon beam in the horizontal plane. By adding nitrogen to the discharge, the number of oxygen atoms was seen to increase considerably. Best performance of the discharge, giving a yield of approximately 50% atomic species, was achieved at an oxygen-to-nitrogen pressure ratio of about 5 to 2. Differential pumping of the ionization chamber resulted in a total pressure of 2×10^{-2} Pa in the interaction region, which excludes a pressure broadening of the spectral features. A Lexane window that was introduced between the interaction chamber and the monochromator maintained the ultrahigh vacuum in the monochromator. The window did not introduce any structure in the vicinity of the K edge of oxygen, as determined in an auxiliary ion-yield spectrum with no oxygen present. The photon energy scale was calibrated with respect to the well-known O $1s \rightarrow \pi^*$ resonance in CO at 534.21 eV [18,19] by using mixtures of CO, O_2, and O.

Figure 1 gives an overview of the region of the Rydberg resonances and illustrates the procedure used for determining

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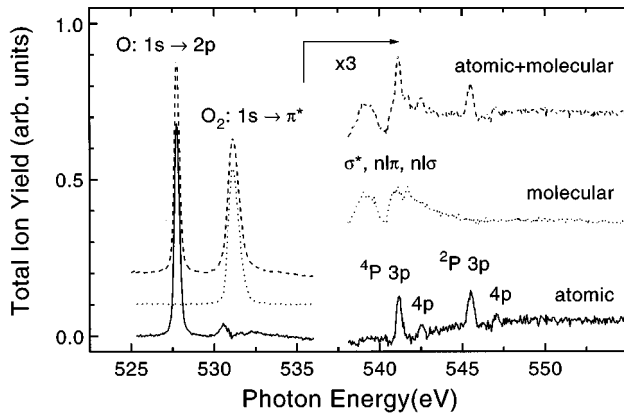
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FIG. 1. Ion-yield spectrum of the $1s \to np$ excitations in atomic oxygen, recorded with moderate resolving power (bandwidth 250 meV). The upper spectrum shows a superposition of the molecular and atomic spectra as recorded. In the lower spectrum, the O_2 contribution (middle, discharge off) is subtracted.

TABLE I. Theoretical energies (in eV) and relative intensities of the six transitions contained in the $1s \to 2p$ resonance at 527.85 eV.

Transition	Energy	Rel. Energy [a]	Rel. Intensity [a]
$^3P_2 \to {}^3P_2$	528.1241	0	1
$^3P_2 \to {}^3P_1$	528.1550	0.031	0.3333
$^3P_1 \to {}^3P_2$	528.1066	-0.018	0.1143
$^3P_1 \to {}^3P_1$	528.1375	0.013	0.0227
$^3P_1 \to {}^3P_0$	528.1533	0.029	0.0091
$^3P_0 \to {}^3P_1$	528.1289	0.005	0.0023

[a]Normalized to the strongest transition.

the atomic ion yield. Two spectra, one with discharge on, and another with discharge off were recorded. The atomic spectrum is isolated by subtracting the molecular spectrum, using the intensity of the $1s \to \pi^*$ peak for normalization. The main resonance $1s \to 2p$ at 527.85(10) eV and higher Rydberg members $n=3,4$, converging to the ^4P and ^2P thresholds, respectively, are clearly seen. The continuous background in the spectrum amounts to 20% of the $1s \to 2p$ peak intensity with the discharge on. As known from previous measurements [17], the discharge also produces NO and molecular oxygen in the metastable $^1\Delta$ state. We found that NO makes no discernible contributions, while metastable O_2 is assumed to be responsible for the residual peak at 530.5 eV.

Spectra were recorded at photon bandwidths ranging from 57 to 270 meV full width at half maximum. The use of
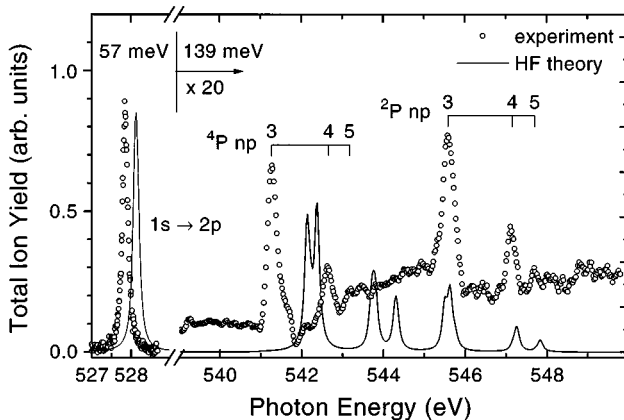
different slit settings of the monochromator, and repetitions of the measurements, allowed us to verify the original calibration [16] of the resolving power and, at the same time, assess deviations due to possible beam line instabilities. One of the high-resolution spectra is displayed in Fig. 2. The nearly Lorentzian contour of the $1s \to 2p$ peak shows that the bandwidth makes a small contribution only, whereas the contours of the higher members may indicate the presence of multiplets. The sources of the minor fluctuations cannot be identified with certainty.

Under the assumption that the $1s \to 2p$ peak represents a single line, we fitted the peak with a single Voigt profile and extracted a Lorentzian width of 143 meV. This would normally be regarded as the linewidth for this transition. However, in the open-shell configuration of O, this peak consists of six transitions connecting the multiplets of the initial and final states:

$$1s^2 2p^2 2p^4 (^3P_{0,1,2}) + h\upsilon \to 1s^1 2p^2 2p^5 (^3P_{0,1,2}).$$

In order to estimate the influence of the fine structure on the width of the resonance, we performed an *ab initio* calculation using a Hartree-Fock program [20]. For the ground state we used a single $2s^2 2p^4$ configuration, while for the excited state, configuration interaction (CI) between the $2s^2 2p^4 np, n=3-5$, basis states was taken into account. If the oxygen atom were in its ground state, $2p^4 (^3P_2)$, only two transitions, split by 31 meV and having an intensity ratio of 3:1, would be active. However, in addition to the

FIG. 2. High-resolution ion-yield spectrum of the $1s \to np$ excitations in atomic oxygen, recorded with a bandwidth of approximately 57 meV for the $1s \to 2p$ transition (left) and 139 meV for the higher Rydberg members. The solid curve represents a Hartree-Fock calculation of energies and relative intensities, convoluted with the total linewidth and normalized to the intensity of the $1s \to 2p$ transition. The continuous part of the spectrum above the ^4P threshold at 543.9 eV was not calculated.
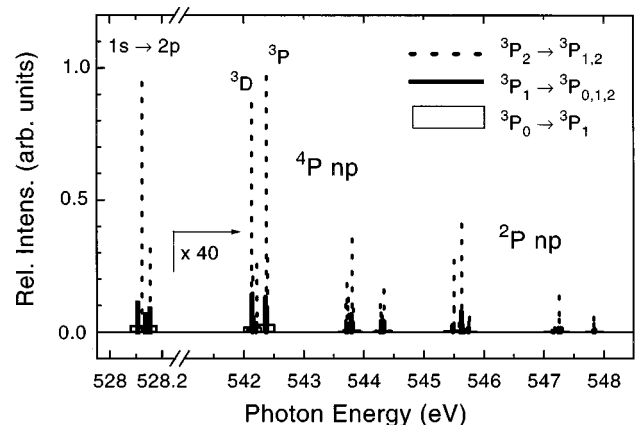

FIG. 3. Bar diagram of the relative transition intensities from a CI Hartree-Fock calculation. The relative populations of the initial states $I(^3P_2)$, $I(^3P_1)$, and $I(^3P_0)$ were taken into account.

TABLE II. Comparison of experimental and theoretical energies and relative intensities of the two Rydberg series converging to the ^4P and ^2P limits of atomic oxygen.

Configuration	Energy (eV)		Relative Intensity	
	Expt.	Th.	Expt.	Th.
$1s^12s^22p^5(^3P)$	527.85(10)[a]	528.13	100	100
$1s^12s^22p^4(^4P)3p$	541.27(15)	542.27	6.2(6)	5.1
$1s^12s^22p^4(^4P)4p$	542.67(15)	543.76	1.6(2)	1.9
$1s^12s^22p^4(^4P)5p$	543.18(15)	544.30	0.36(5)	1.1
$1s^12s^22p^4(^2P)3p$	545.59(15)	545.62	5.4(6)	2.0
$1s^12s^22p^4(^2P)4p$	547.16(15)	547.24	1.9(2)	0.5
$1s^12s^22p^4(^2P)5p$	547.71(15)	547.85	0.36(5)	0.24

[a]Calibrated with reference to CO: O$1s \rightarrow \pi^*$ at 534.21 eV, given in [19]. The error in the reference is not included.

$2p^4(^3P_2)$ ground state, the $2p^4(^3P_1)$ and $2p^4(^3P_0)$ excited states are also populated, with ratios of $I(^3P_2):I(^3P_1):I(^3P_0) \approx 1:0.34:0.09$ under the conditions of the discharge [21]. These ratios are used to adjust the theoretical transition rates of the excited states; the weighted relative rates are given in Table I.

Based on this information, the $1s \rightarrow 2p$ contour for each spectrum was then fitted by six Voigt profiles of equal width and proper spacing. These fits were rather insensitive to variations of about 10% applied to the energy spacings and relative intensities, and resulted in an improved χ^2 compared to the one-line fit. A Lorentzian linewidth of 140(9) meV was obtained by averaging over the widths derived from 17 separate spectra with different slit settings. The error of ± 9 meV is based on the Gaussian distribution (one standard deviation) of the width measurements. It is to be noted that the *difference* of about 3 meV between the single line and the multiline fits is not subject to the total error of 9 meV.

The linewidth of 140(9) meV, derived primarily from experiment, compares with the theoretical values of 169 meV, obtained in a multiconfigurational Hartree-Fock (MCHF) calculation [22], and values of 135 and 139 meV, obtained in an S-matrix calculation [23]. In spite of this considerable discrepancy, both calculations give satisfactory agreement with the experiment [24,25] for the various Auger rates of the O atom, with the MCHF results [22] being somewhat superior to the S-matrix results [26].

By definition, the natural level width pertains to the *ionization* of an electron from that level. Hence, the natural K-level width in the $[1s]2s^22p^4$ configuration is not equivalent to the linewidth we report. An estimate for the K width might be made by a statistical adjustment to the lifetime-defining Auger rate, taking into account the lower valence electron density of the $2p^4$ configuration. However, such an estimate would be quite coarse because the Auger rates depend markedly on the Coulomb field at low Z. Instead, we need to rely on the result of a calculation that agrees well with the width in the $[1s]2s^22p^5$ configuration derived here to yield a good value for the natural K-level width in $[1s]2s^22p^4$. This K-level width must be broken down into the individual widths of the multiplets created by the open-shell structure. According to Petrini and Araújo [26], the calculated Auger widths are $\Gamma(^4P)=126$ meV and $\Gamma(^2P)=109$ meV for O$^+$ with a K electron removed into the continuum [27]. An experimental verification of these

values cannot be obtained from a photoabsorption measurement, as is possible for a closed-shell atom [8], but would have to come from a photoelectron measurement done in the absence of postcollision effects and at extremely high resolution.

Although it would seem that the linewidths of the higher members of the absorption series should be closer to the natural widths of the K-shell ionized atom, they are unsuitable for width determinations because of the dramatically increased multiplet splitting of the possible transitions and ultimately the merging of the highest members into a quasicontinuum [28]. To assess the composition of the higher excitation lines, we extended our calculation to the series members with $n=3-5$. These six members of both series contain 113 lines, even if those lines with an oscillator strength of less than 1×10^{-4} that represent in sum less than 1% of the spectral intensity are neglected. The calculated spectrum is shown in Fig. 3 as a bar diagram of the major lines.

For comparison with the measured spectra, the $1s \rightarrow 2p$ feature was convoluted with a Voigt profile, which has an instrumental (Gaussian) width of 57 meV and a natural (Lorentzian) width of 140 meV, while the $1s \rightarrow np$, $n=3-5$ lines were convoluted with profiles containing a Gaussian width of 139 meV and an *ad hoc* Lorentzian width of 140 meV. The spectrum thus generated is compared in Fig. 2 with the measured spectrum, matching the intensities at the $1s \rightarrow 2p$ peak. A definite correspondence between the experimental and the theoretical spectra is observed. However, the calculation seems to underestimate the splitting between the two Rydberg series leading to the $(^4P)np$ and $(^2P)np$ coupled excited states. As a consequence, while the excitation energies for the ^2P series are in accord with experiment, the ^4P is shifted towards energies about 1 eV too high. Values of the transition energies and relative intensities are summarized in Table II. Surprisingly, for the relative intensity we find a better agreement between experiment and theory for the ^4P series than for the ^2P series. Detailed inspection of the fine structure of the $(^4P)3p$ peak nevertheless shows variances.

In conclusion, we measured and calculated the energies and relative intensities of the excitation series $1s \rightarrow np$ in atomic oxygen. The individual linewidth for the six transitions contained in the $1s \rightarrow 2p$ transition was evaluated to be 140(9) meV. We demonstrated that this value cannot be derived from experimental data alone, but requires theoretical

input on the multiplet splitting and the rates of all possible transitions. We also showed that the natural K-level width in oxygen cannot be deduced from an absorption spectrum. Although for the case of the oxygen atom the multiplets occurring in both the initial and final states play only a small role for the $1s \rightarrow 2p$ transition, multiplets and partial transition rates assume greater importance for the transition to higher excited states and, in many instances, for transitions between core and partially filled subshells in other open-shell elements. Energies and relative intensities of the spectral lines up to $n = 5$ are by and large reproduced by our HF calculation. However, a quantitative agreement with experiment for all relevant parameters remains a challenge to theory.

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