

# Spin-Orbit Coupling in the $\text{O}_2^-$ Anion

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We could resolve the spin-orbit splitting of  $160 \pm 4 \text{ cm}^{-1}$  in the  $^2\Pi$  ground state of  $\text{O}_2^-$  anions by high resolution photodetachment photoelectron spectroscopy. The observed splitting is in good agreement with the theoretically derived value. Our directly measured electron affinity of  $\text{O}_2$  is  $450 \pm 2 \text{ meV}$  and deviates within experiment errors from previous values. kHz repetition rate was applied to avoid space charge and improve electron energy resolution in a time-of-flight electron energy analyzer.

## 1. Introduction

Anion photodetachment spectroscopy is a useful tool to study mass selected atomic [1] and van der Waals clusters [2]. There are several advantages of the photodetachment spectroscopy technique justifying the effort to start with anions: (a) Mass selection prior to spectroscopy allows easy correlation of the measured energy spectra to the corresponding molecular or cluster species. In this way spectroscopy of the neutral ground state of mass selected clusters can be performed by photodetachment. (b) Multiple quanta of either intra- or intermolecular vibrations can be excited in contrast to IR spectroscopy. (c) Transition states of unstable extremely short lived neutral complexes can be studied because photodetachment is a prompt process [3].

ZEKE spectroscopy (Zero Kinetic Energy electron detection), developed for spectroscopy of cations, i.e. ionization of neutrals [4], can as well be applied for anions to achieve high resolution down to  $4 \text{ cm}^{-1}$  [2]. In contrast to ionization of neutrals, cross sections at the onset can be very low for p- or d-wave photodetachment ( $l=1,2$ ), as predicted by Wigner [5]. Thus, as a consequence, the onset behavior of p-wave photodetachment can prevent the application of ZEKE spectroscopy [6]. In  $\text{O}_2$ , for the  $\text{O}_2^- \ ^2\Pi_g \rightarrow \text{O}_2 \ ^3\Sigma_g^-$  transition p-wave photodetachment is prevalent. Therefore we applied conventional high resolution photoelectron spectroscopy with photoexcitation far above detachment threshold in order to overcome this problem.

$\text{O}_2^-$  photodetachment spectra have been recorded previously [7–13], but as far as we know we are the first to resolve the spin-orbit splitting of the anion ground state.

## 2. Experimental

$\text{O}_2^-$  anions have been produced by attachment of low energy secondary electrons formed by high energy electrons (energy about 1.0 keV) in a supersonic expansion (continuous nozzle, 50  $\mu\text{m}$  nozzle diameter, 5 bar:  $\text{O}_2/\text{N}_2=1/5$ ). Anions are extracted perpendicular to the supersonic beam by a pulsed electric field and transferred into a second vacuum chamber (background pressure  $10^{-7}$  mbar) through an orifice of 1.5 mm. Mass selection is performed in a quadrupole mass spectrometer ( $m/\Delta m > 400$ ). After mass selection the  $\text{O}_2^-$  anions are accelerated and focussed into a  $\mu$ -metal shielded time-of-flight photoelectron spectrometer ( $l=47 \text{ cm}$ , surface covered with graphite). Photodetachment at  $\text{O}_2^-$  anions is performed by collinear laser excitation with either the fundamental (1047 nm, 0.5 mJ/pulse) or the second harmonic (523.5 nm, 0.2 mJ/pulse) of an Nd:YLF laser (repetition rate up to 10 kHz, pulse duration 7 ns, TFR, Spectra Physics). Photoelectron spectra are recorded by measuring the time-of-flight of photoelectrons emitted perpendicular to the ion velocity. Flight time measurement for photodetached electrons was performed by single particle detection (MCP detector in combination with a constant fraction discriminator) and a start-stop logic. The accuracy of the time measurement was mainly limited by the laser pulse of 7 ns. As a result of this, the electron energy resolution varies

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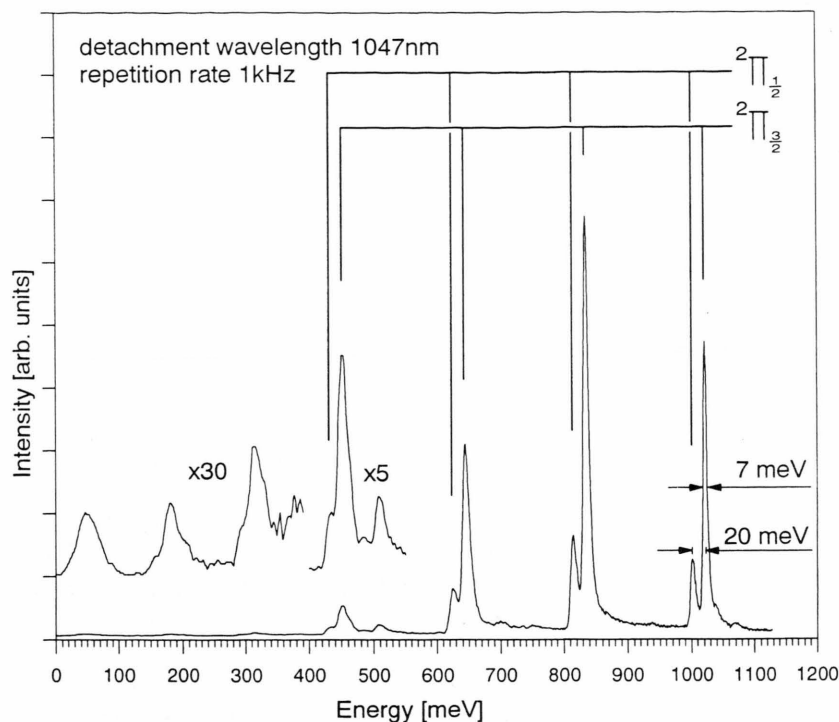


Fig. 1. Conventional photodetachment photoelectron spectrum of  $O_2^-$ :  $O_2^- 2\Pi_g \rightarrow O_2^- 3\Sigma_g^-$  transition. The photodetachment wavelength was 1047 nm. Here the zero point of the energy scale is chosen to be the anion ground state.

with electron energy between 7 meV and 20 meV. Our best resolution in electron energy of 3.5 meV was achieved for  $O^-$  anion photodetachment by observing the spin-orbit multiplett [13] at an absolute electron energy of about 60 meV. For this experiment a kHz-ns-Ti:Sapphire laser was used. The conceptional idea of the high repetition rate was reduction of space charge for each cycle while keeping a high total number of events per second. A typical anion number per cycle was  $10^4$  at a repetition rate of 1 kHz. For the conversion of the time-of-flight spectra to energy spectra, the ion velocity and the nonlinear transformation of intensities has been taken into account. The cut-off in electron energy for our instrument is 40 meV.

### 3. Results and Discussion

Our photodetachment spectrum of  $O_2^-$  is shown in Fig. 1, and the corresponding energy level scheme is presented in Figure 2. In both figures the origins of the energy scales corresponds to the anion ground state. The spectrum of Fig. 1 shows the vibrational structure of the  $3\Sigma_g^-$  ground state of neutral  $O_2$ . On

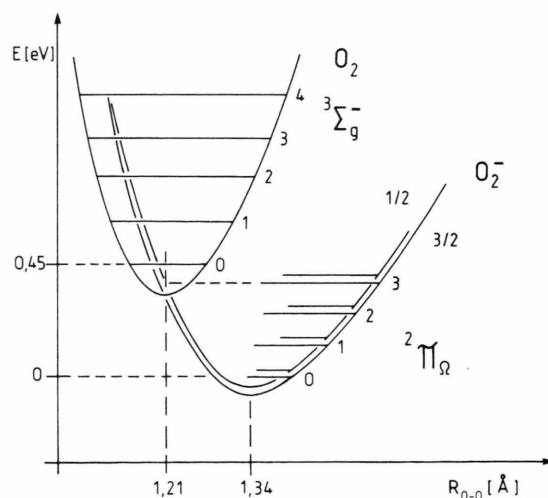


Fig. 2. Energy level scheme of the potential curves of  $O_2$  and  $O_2^-$ . The transitions from the upper spin-orbit component  $2\Pi_{1/2}$  in  $O_2^-$  are shifted to lower energies. Note that the observed third vibrational quantum state of the anion is just below the detachment threshold.

the right side of Fig. 1 some weak hot band transitions are displayed in magnification. For each strong transition clearly a small prestructure can be resolved at an energy distance of  $-20 \text{ meV}$  ( $-160 \text{ cm}^{-1} \pm 4 \text{ cm}^{-1}$ ). We contribute this double structures to transitions to the same quantum number  $n$  in the neutral  $^3\Sigma_g^-$  state, but starting either in the lower ( $\Omega=3/2$ ) or the upper component ( $\Omega=1/2$ ) of the spin-orbit doublet of the  $^2\Pi$  anion ground state of  $\text{O}_2^-$  (see Figure 2). Several experimental findings sustain this assignment:

- The energy spacing between pairs of corresponding transitions is found to be constant. If the prestructure were due to a hot band transition, energy differences between neighbored peaks, i.e. hot and cold bands should change over the spectrum due to the different energy shifts caused by the anharmonicity of the upper electronic state ( $\omega_e x_e = 12.07 \text{ cm}^{-1}$ ).
- The absolute value of the energy shift of the above prestructure is  $160 \pm 4 \text{ cm}^{-1}$  and thus close to the estimated value for the  $^2\Pi$  ground state of  $\text{O}_2^-$  (see below). The shift of the prestructure to lower energy in the photoelectron spectrum then corresponds to the higher initial energy (see Figure 2).
- Intensities of the prestructures are large in comparison to the hot band transitions shown on the left side of Fig. 1 but small in comparison to the main transitions. This, however, could fit to an initial anion population of the upper spin-orbit component of the  $^2\Pi_g$  anion ground state of  $\text{O}_2^-$ . From the intensities we calculate an electronic “temperature” of  $T_{\text{el.}} = 160 \text{ K}$ , which is in reasonable agreement with similar experiments [6].
- The intensity ratio between both structures is in good approximation constant over the whole spectrum. If hot bands were involved, the intensity distribution of the hot band spectrum should peak differently compared to the cold band spectrum due to different Franck-Condon factors for hot and cold band transitions.

Spin-orbit splitting energy of small linear molecules and molecular ions can be calculated by  $E = E_0 + \zeta A \Sigma$  [15], where  $E_0$  is the energy in absence of the spin-orbit splitting,  $A$  is the electronic angular momentum (for  $\text{O}_2^-$ :  $A=1$ ),  $\Sigma$  is the spin angular momentum (for  $\text{O}_2^-$ :  $\pm 1/2$ ) and  $\zeta$  is the molecular spin-orbit interaction parameter. This molecular spin-orbit interaction parameter  $\zeta$  can be derived in good approximation from the atomic spin-orbit coupling parameters  $\zeta_{\mu\text{O}}$  given for several atoms by Eland [15]: The molecular spin-orbit

interaction parameter is calculated as the sum over the weighted atomic spin-orbit interaction parameters. Thereby the weighting factor is the coefficient of the according atomic orbital in the linear expansion of the highest occupied molecular orbital by atomic orbitals [15]. For the homonuclear  $\text{O}_2^-$  molecule follows  $\zeta = 2 c^2 \zeta_{\mu\text{O}}$ . For an antibonding  $\pi$  orbital  $c^2$  can be calculated as  $1/(2-2S)$ , where  $S$  is the overlap integral of the involved atomic orbitals. With  $\zeta_{\mu\text{O}} = -0.019 \text{ eV}$  and an overlap integral value of  $S=0$  the molecular spin-orbit splitting in  $\text{O}_2$  ( $\Delta E = 2\zeta A \Sigma$ ) would be  $-19 \text{ meV}$ . This is in good agreement with our value of  $-20 \text{ meV}$ . The slight difference to the experimental value can be explained by the contribution of the atomic overlap integral of the atomic  $2p_x$  orbitals. Note that the sign of the spin-orbit splitting is negativ, which shows that the spin-orbit components are inverted, the  $\Omega=3/2$  being the lowest state. In general, the good agreement of theory and experiment confirms the high validity of the ansatz in [15].

Our peak position of the  $\text{O}_2^- \ ^2\Pi_{3/2} \rightarrow \text{O}_2 \ ^3\Sigma_g^-$  transition is  $450 \pm 2 \text{ meV}$ , in good agreement with the value of  $451 \text{ meV}$  found by Travers et al. [9]. They extrapolated their photodetachment onset by taking into account the shift of position by the rotational envelope (the rotational temperature in their experiment was  $600^\circ\text{C}$ ) and the non-resolved spin-orbit splitting. For the determination of the electron affinity of  $\text{O}_2$  we did not take into account rotational effects because of the low rotational temperature we believe to have due to our supersonic expansion.

For the ground state of  $\text{O}_2^-$  we find a vibrational frequency of  $1110 \text{ cm}^{-1}$  ( $\pm 25 \text{ cm}^{-1}$ ) by analysis of the hot band positions. This value is larger than that found by Travers et al. ( $1073 \text{ cm}^{-1} \pm 50 \text{ cm}^{-1}$ ), but still in the error margin.

It is worth to note that the third vibrational quantum state of both spin-orbit components of the anion are still below the neutral ground state  $^3\Sigma_g^-$ , as shown in Figure 2. In spite of the high vibrational energy corresponding to this levels, we clearly observe this overtone in our photodetachment spectrum as shown in the magnified part on the left hand of Figure 1. We believe these high vibrational quantum states to be populated not thermally but by collisions in the extraction region. Hot band transitions due to anions vibrationally excited to energies above the electron detachment threshold have not been observed. Contributions due to a population of the first electronic excited anion state  $^4\Sigma_g^-$ , which is thought to be just

below the detachment threshold [14], have not been observed in our spectra.

The equilibrium O–O distance, the vibrational frequency and the anharmonicity are well known for neutral  $\text{O}_2$  in the  $^3\Sigma_g^-$  state [16]. Therefore the equilibrium O–O distance of the anion can in principle be calculated by Franck-Condon simulations using the photodetachment intensities, as done by Celotta et al. ( $R_{\text{O-O}} = 1.341 \text{ \AA}$ ) [7] and Travers et al. ( $R_{\text{O-O}} = 1.347 \text{ \AA}$ ) [9]. However the individual vibronic transition intensities may depend on photodetachment cross sections due to the different photon excess energies [14]. It should be noted here that our intensities of vibronic transitions in spectra taken at photon energies of 1.16 eV (1047 nm) differ considerably from peak intensities found at higher excess energies [7, 9]. The anisotropy may as well change with the vibrational quantum number of the neutral  $^3\Sigma_g^-$  state [7] and may thus influence the intensities. Therefore we cannot estimate the influence of our new value of the  $\text{O}_2^-$  frequency on Franck-Condon simulations.

Spin-Orbit coupling in either the anion or the neutral is generally complicating spectroscopy by photodetachment. Spin-orbit interaction is also disturbed by complexation, as for example observed in weakly bound molecular clusters as  $\text{I}^-\text{CO}_2$  [2]. The situation

is especially complicated in homomolecular dimer complexes: As discussed in detail by Otha et al. [17], spin-orbit splitting of the  $\text{O}_2^-$  monomer significantly influences the manifold and stability of the electronic states of the anion dimer  $(\text{O}_2)_2^-$ : A large variety of electronic states can be generated by interaction of the spin-orbit states of both  $\text{O}_2$  molecules.

#### 4. Conclusion

In our photodetachment photoelectron spectrum of  $\text{O}_2^-$  we achieved an electron energy resolution below 10 meV for low energy electrons and observed a spin-orbit splitting of  $160 \text{ cm}^{-1}$ , which is in good agreement with the calculated value. Previous values of the electron affinity have been confirmed, and an accurate vibrational frequency of the anion ground state is given.

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