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Cooper minima and circular dichroism in photoelectron angular distributions

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Resonance enhanced multiphoton ionization (REMPI) combined with high-resolution angle-resolved photoelectron spectroscopy (ARPES) has in recent years been shown to be a sensitive probe of excited molecular states and their photoionization dynamics.¹⁻⁵ We have previously shown that circular dichroism exists in the photoelectron angular distributions (CDAD) from aligned molecules, that it arises in the electric dipole approximation, and that it is of a measurable magnitude.⁶⁻⁹ CDAD has since been experimentally measured,¹⁰ and was subsequently used to determine the alignment of photodissociated molecular fragments.¹¹ We have also more recently demonstrated that the presence of Cooper minima will give rise to strong non-Franck-Condon behavior in vibrationally resolved REMPI,^{12,13} and, under certain circumstances, a strong rotational selectivity in ion distributions.¹⁴ Cooper minima have been widely studied theoretically and experimentally in atoms and in molecular ground states,¹⁵⁻¹⁷ but have only recently been observed experimentally in optical double resonance spectroscopy of highly excited Rydberg states of NO.¹⁸ The larger number of partial waves contributing to molecular photoionization compared to atomic photoionization makes it difficult to locate Cooper minima in the total cross sections. A Cooper minimum has yet to be observed from ionization via an excited molecular Rydberg state.

In this Communication we illustrate how the method of CDAD can be used to uniquely locate and identify Cooper minima in photoionization of aligned molecular excited states even when these minima are present in only one of the possible photoionization channels. The CDAD spectrum of such a state, being a difference between two angular distributions, will be seen to go through a zero near the Cooper minimum and to change sign. As a specific example of this behavior we present results of *ab initio* calculations for $(1 + 1')$ REMPI of the optically aligned $D^2\Sigma^+(3p\sigma)$ state of NO. Previous high-resolution experiments and calculations for REMPI via the $D^2\Sigma^+(3p\sigma)$ state have shown the ionic rotational branching ratios to be very energy dependent, and indicative of a possible non-

adiabatic interaction between the $v_D = 0$ level and the $v_A = 4$ level of the lower lying $A^2\Sigma^+(3s\sigma)$ state.⁵ This interaction will be ignored here, but can be incorporated in a fashion similar to our previous work.⁵ The observed strong energy dependence of the rotational branching ratios on photoelectron energy is predominantly due to a Cooper minimum in the d wave ($l = 2$) of the $k\pi$ continuum around 3.2 eV (not shown).

Due to their weak influence on total cross sections, Cooper minima have traditionally been detected in photoelectron angular distributions.¹⁷ Cooper minima are more pronounced in photoelectron angular distributions since the interference between various ionization channels changes rapidly around the minimum.¹² As an ARPES technique, CDAD is expected to display this sensitivity. Here the CDAD signal is defined as the difference between the angular distributions resulting from preparation of an aligned resonant intermediate state with linearly polarized light and subsequent ionization with left and right circularly polarized light, respectively, i.e., $I^{\text{CDAD}}(\Theta) = I^{\text{L}}(\Theta) - I^{\text{R}}(\Theta)$.⁶ We have previously shown that for photoionization of a state aligned by absorption of one photon of linearly polarized light, the CDAD signal can be written as⁹

$$I^{\text{CDAD}}(\Theta) = \frac{1}{2}A_2\overline{\beta}_2 \sin(2\Theta), \quad (1)$$

where A_2 is the alignment quadrupole moment for the resonant intermediate state and $\overline{\beta}_2$ contains information about the photoionization dynamics. In the $(1 + 1')$ CDAD experiment proposed here, the alignment A_2 of the intermediate state remains fixed while the value of $\overline{\beta}_2$ changes with the wavelength of the ionizing laser.

Figure 1 shows the calculated CDAD signal for $(1 + 1')$ REMPI via the $R_{21}(5.5)$ branch of the $D^2\Sigma^+$ state of NO at various photoelectron kinetic energies. The electronic wave function of the $D^2\Sigma^+(3p\sigma)$ state of NO and the photoelectron continuum orbitals were determined as explained previously.⁵ The CDAD signal is found to

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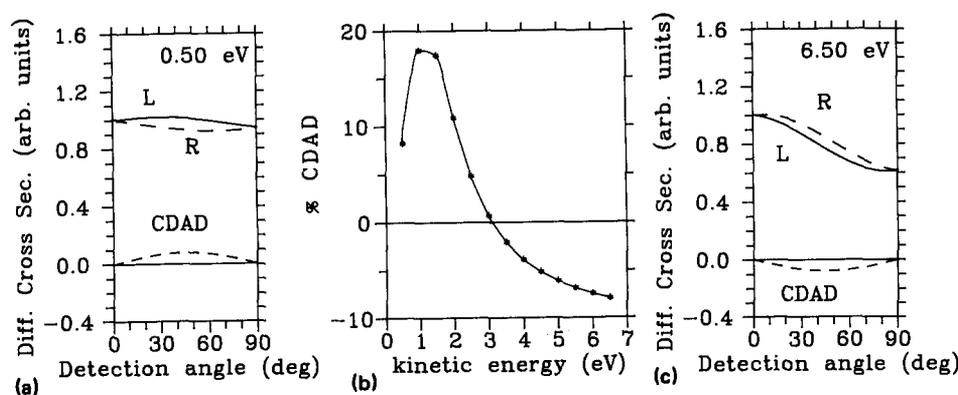


FIG. 1. (a) Normalized differential cross section vs collection angle for $(1 + 1')$ REMPI via the $R_{21}(5.5)$ branch of the $D^2\Sigma^+(3p\sigma)$ state of NO for left (L) and right (R) circularly polarized light and CDAD for a photoelectron kinetic energy of 0.5 eV. (b) Percent CDAD signal $[I^{CDAD}(\Theta = 45^\circ)/I^{L,R}(\Theta = 0^\circ) \times 100]$ as a function of photoelectron kinetic energy. (c) Same as Fig. 1 (a), but for a photoelectron kinetic energy of 6.5 eV.

have the predicted $\sin(2\Theta)$ angular dependence and to flip sign through the Cooper minimum region near 3.2 eV.

These results can be explained on the basis of an atomic model for CDAD. Single-center expansion of the 7σ ($3p\sigma$) orbital around the center-of-mass at an internuclear separation of 2.0069 a.u. gives a partial wave composition of 0.6% s , 99.2% p , and 0.1% d character, consistent with earlier calculations.¹⁹ This result suggests the CDAD behavior might be thought of as photoionization from an aligned atomic p orbital. In this case photoionization would lead to ks and kd continuum channels. CDAD has been shown to arise solely from interference between these two channels,²⁰ i.e., $\bar{\beta}_2$ takes the form,

$$\bar{\beta}_2 \propto \langle 3p|r|ks \rangle \cdot \langle 3p|r|kd \rangle \cdot \sin(\delta_s - \delta_d), \quad (2)$$

where $\langle 3p|r|kl \rangle$ is the radial matrix element for photoionization of a $3p$ orbital into the l continuum and δ_l is its phase shift. From this equation it can be seen that CDAD will change sign whenever one of the radial matrix elements goes through zero and flips sign (Cooper minimum) or the phase shift difference goes through $n\pi$, where $n = 0, 1, 2, 3, \dots$. In the present case, the d partial wave ($l = 2$) in the molecular $k\pi$ continuum channel goes through a Cooper minimum near 3.2 eV. This result explains the change in sign of the CDAD spectra shown in Fig. 1.

It must be emphasized that CDAD will go through zero at the exact position of the Cooper minimum only for atoms. For molecules, other continuum channels, such as the p ($l = 1$) partial wave, contribute to the cross section as well due to "rescattering" by the nonspherical molecular ion potential. These contributions result in a background CDAD signal which should shift the position of the CDAD zero from that of the true Cooper minimum. The best we can say, then, is that the CDAD signal will flip sign near a Cooper minimum in the molecular case.

In conclusion, we note that this application of the CDAD technique for detection of molecular Cooper minima is quite general, and that the Cooper minimum should be readily observable from the CDAD signal for $(1 + 1')$ REMPI via the $D^2\Sigma^+$ state of NO.

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