

## Observation of circular dichroism in photoelectron angular distributions

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Citation: *The Journal of Chemical Physics* **85**, 6803 (1986); doi: 10.1063/1.451412

View online: <http://dx.doi.org/10.1063/1.451412>

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## COMMUNICATIONS

## Observation of circular dichroism in photoelectron angular distributions

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(Received 8 September 1986; accepted 1 October 1986)

In a series of recent papers, Dubs, Dixit, and McKoy<sup>1-4</sup> have theoretically explored the possibilities of using photoelectron angular distributions resulting from ionization with circularly polarized light to probe the orientational properties of excited or chemisorbed atoms and molecules. In particular, these authors have shown<sup>3,4</sup> that circular dichroism in photoelectron angular distributions (CDAD) should be a sensitive probe of molecular excited alignment, i.e., the non-statistical distribution of  $|JM_J\rangle$  levels, produced by photon or particle impact, external fields, photofragmentation, or surface scattering. In this Communication, we present results of a two-color, two-polarization CDAD study of the  $A^2\Sigma^+(v=0)$  excited state of NO for which dichroic effects are observed for the first time.

The pump-probe process studied in this work can be written as  $\text{NO}(X^2\Pi_{1/2}, v''=0, J''=\frac{1}{2}) + 2\gamma(450\text{--}452\text{ nm, linearly polarized}) \rightarrow \text{NO}^*(A^2\Sigma^+, v=0, J) \xrightarrow{\text{NO}^*(A^2\Sigma^+, v=0, J) + \gamma'(266\text{ nm, circularly polarized})} \text{NO}^+(X^1\Sigma^+, v'=0) + e^-$ , where the two-photon excitation process is used to prepare an aligned distribution of  $|JM_J\rangle$  substates and the one-photon ionization with circularly polarized light probes this alignment. A CDAD curve is generated by taking the difference between photoelectron angular distributions (defined as the photoelectron intensity vs the angle between the linear polarization vector of the pump radiation and the electron propagation direction) for right and left circular polarization of the ionizing (266 nm) radiation. A detailed description of the apparatus and time-of-flight (TOF) electron spectrometer will be published elsewhere.<sup>5</sup> Briefly, counter-propagating pump (450–452 nm) and probe (266 nm) laser beams obtained from a Nd:YAG-pumped dye laser system were focused onto a molecular beam containing rotationally cold ( $T_R \sim 5\text{ K}$ ) NO target molecules. Both laser beams were linearly polarized via prism polarizers after which the 266 nm light was circularly polarized with a 1/4-waveplate. Rotation of the linear polarization vector of the 450 nm pump radiation was accomplished through the use of a Babinet–Soleil compensator mounted on a rotation stage.

Experimental CDAD results for  $(2+1)$  REMPI via the  $R_{21} + S_{11}(1/2)$  and  $S_{21}(1/2)$  rotational branch lines are shown in Fig. 1. The data are plotted as the ratio of the CDAD intensity relative to the intensity of the differential cross section at  $\theta = 0^\circ$  where both the left and right angular distributions are equal by symmetry.<sup>3,4</sup> Inspection of Fig. 1 shows that the experimental CDAD signal is well beyond statistics (as judged by the scatter of the data points) and approaches 20% of the circularly polarized differential cross section. The symmetry and sign change of the data about  $0^\circ$  are the earmarks of dichroic effects in photoionization from aligned target states.<sup>1,3</sup>

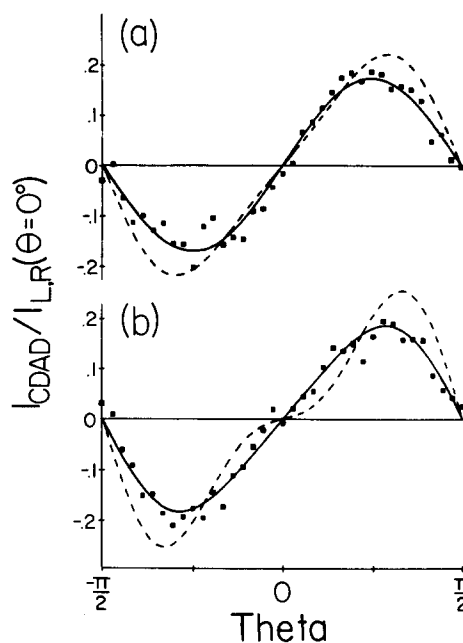


FIG. 1. CDAD intensity for  $(2+1)$  REMPI of the  $A^2\Sigma^+, v=0$  level of NO via (a) the  $R_{21} + S_{11}(1/2)$  and (b) the  $S_{21}(1/2)$  rotational branch lines;  $\blacksquare$ , experimental data points; —, least-squares fit to  $a_2P_2^{1/2} + a_4P_4^1$  (see the text); ---, theoretical calculations of Dubs, Dixit, and McKoy (Ref. 3).

The solid lines in Fig. 1 are least squares fits of the CDAD data to the summation  $\sum_L a_L P_L^1(\cos \theta)$ , which describes CDAD distributions taken with the experimental arrangement used in this work.<sup>3,4</sup> The  $P_L^1(\cos \theta)$  are associated Legendre polynomials of order  $L$  ( $M = 1$ ) and  $\theta$  is the angle between the linear polarization and electron propagation vectors. Symmetry considerations restrict  $L$  to even values in the range  $2 \leq L \leq 2J$ , where  $J$  is the smaller of the two quantities: the total angular momentum of the probed state or the number of linearly polarized pump photons. The expansion coefficients  $a_L$  are actually products of two other parameters,  $A^{(L)}$  and  $\beta_L$ , which describe the alignment of the excited state and the ionization dynamics of the bound-continuum transition, respectively.<sup>4</sup> For the spin-unresolved  $R_{21} + S_{11}(1/2)$  rotational branch line ( $J = 3/22(R), 5/2(S), N = 2$ ),<sup>6</sup> the CDAD data was found to be well described by only the first term in the expansion, i.e.,  $a_2 P_2^1(\cos \theta)$  [see Fig. 1(a)]. In contrast, the  $S_{21}(1/2)$  branch line ( $J = 5/2, N = 3$ ) required the full  $a_2 P_2^1 + a_4 P_4^1$  expansion to adequately fit the data with  $a_4/a_2 = -0.08(2)$ . Inclusion of the  $L = 4$  term is clearly visible in Fig. 1(b) as the fitted CDAD distribution is no longer symmetric about  $\pm \pi/4$ .

Whereas the fit of the experimental  $R_{21} + S_{11}(1/2)$  CDAD data indicated a very small  $L = 4$  component, the calculations of Dubs *et al.*<sup>3</sup> (shown as dashed lines in Fig. 1) result in a  $a_4/a_2$  ratio of  $-0.12$  which breaks the  $\pm \pi/4$  symmetry of the CDAD curve. For the  $S_{21}(1/2)$  branch line [Fig. 1(b)], the calculations predict a larger  $L = 4$  contribution of the CDAD curve ( $a_4/a_2 = -0.27$ ) than that extracted from the experimental fit, however, the overall shift of the CDAD intensity maximum towards  $\pm \pi/2$  is clearly reproduced by experiment. Furthermore, the increase in the

$L = 4$  component in going from the  $R_{21} + S_{11}(1/2)$  to the  $S_{21}(1/2)$  branch line is consistent with the observed CDAD curves. It should be emphasized that the normalization used to plot the CDAD curves in Fig. 1, i.e.,  $I_{\text{CDAD}}/I_{L,R}(\theta = 0^\circ)$ , places the comparison of the calculations and experiment on a quantitative basis. The overall good agreement between the theoretical and experimental CDAD amplitudes suggest that the bound-free ionization dynamics are realistically treated in the theoretical model of Dubs and co-workers. Experimental improvements in laser beam overlap and shot-to-shot power stabilities should increase the statistical quality of these measurements and thereby permit a more detailed comparison of the shapes of the CDAD distributions with theoretical predictions.

The authors are indebted to Dr. Sham N. Dixit, Richard L. Dubs, and Professor Vincent McKoy for helpful discussions and for providing details of their calculations. This work was performed at Brookhaven National Laboratory and was supported by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Physics under Contract No. DE-AC02-76CH00016.

<sup>a)</sup> Support provided by the Donors of the Petroleum Fund, administered by the American Chemical Society.

<sup>1</sup>R. L. Dubs, S. N. Dixit, and V. McKoy, *Phys. Rev. Lett.* **54**, 1249 (1985).

<sup>2</sup>R. L. Dubs, S. N. Dixit, and V. McKoy, *Phys. Rev. B* **32**, 8389 (1985).

<sup>3</sup>R. L. Dubs, S. N. Dixit, and V. McKoy, *J. Chem. Phys.* **85**, 656 (1986).

<sup>4</sup>R. L. Dubs, S. N. Dixit, and V. McKoy, *J. Chem. Phys.* (to be published).

<sup>5</sup>J. R. Appling and M. G. White (to be published); see also W. A. Chupka, A. M. Woodward, S. D. Colson, and M. G. White, *J. Chem. Phys.* **82**, 4880 (1985).

<sup>6</sup>The  $A^2\Sigma^+, v = 0$  level is well described by Hund's case (b) coupling in which  $J = N \pm 1/2$  where  $N$  is the rotational quantum number. The spin-doublets cannot be resolved with the present laser system.

## Reaction kinetics on clusters and islands<sup>a)</sup>

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(Received 2 July 1986; accepted 29 September 1986)

Our Monte Carlo simulations yield anomalously high reaction orders ( $X = 20$  or higher) for *elementary* binary reactions on finite percolation clusters and monodisperse island ensembles. We find good agreement with exciton fusion reactions on naphthalene percolation clusters in isotopic mixed crystals. This has important implications for very-low-dimensional (zero to unity) heterogeneous kinetics.

The elementary binary reaction  $A + A \rightarrow \text{Products}$  has been of much interest recently<sup>1-10</sup> in connection with the problems of heterogeneous chemical kinetics. For instance,<sup>10-13</sup> a nonclassical behavior has been demonstrated for the reaction order  $X$ , defined by

$$R = K[A]^X, \quad (1)$$

where  $R$  is the steady-state reaction rate,  $[A]$  the steady-state reactant concentration, and  $K$  the rate constant. Specifically, instead of the classical result of  $X = 2$ , values of 2.45, 2.5, and 3 have been obtained for the Sierpinski gasket, the critical percolation cluster and the one-dimensional lattice, respectively.<sup>11-13</sup> This problem is of direct interest to chemical reactions and to exciton fusion (annihilation),<sup>1-13</sup> and of indirect interest to radiation damage in semiconductors, electron-hole recombination, biological population studies, and matter-antimatter distribution in the universe.<sup>14</sup> In fact, four years ago<sup>5</sup> it was claimed that triplet exciton fusion in isotopic mixed naphthalene crystals showed  $X$  values up to 20 or higher for a certain alloy concentration range. This was interpreted in terms of guest clus-