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# Reevaluation of the Use of Photoelectron Angular Distributions as a Probe of Dynamical Processes: Strong Dependence of Such Distributions from $S_1$ Paradifluorobenzene on Photoelectron Kinetic Energy

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Photoelectron angular distributions (PADs) have been measured following the excitation of the  $S_1$  origin band in paradifluorobenzene using a range of ionizing wavelengths and for resolved ion vibrational states. The PADs show a dramatic sensitivity to the photoelectron kinetic energy over an energy range of at least 1 eV from threshold, and almost no sensitivity to any prepared intermediate state alignment. This has important consequences for those studies of intramolecular dynamics that use PADs. We suggest that the observed behavior is caused by a shape resonance in the continuum.

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Photoelectron angular distributions (PADs) have been suggested as useful probes of intramolecular dynamical processes by our group [1,2] and by many others [3–7] because of their sensitivity to electronic symmetry and to the alignment of molecular axes. However, this utility is often reliant on the fact that the photoionization dynamics themselves are not strongly energy dependent so that PADs corresponding to different initial and final vibrational states can be assumed to be similar. In the kinds of experiments designed to probe intramolecular dynamics in this way an intermediate state is usually prepared prior to ionization, and the effect of changing the ionizing wavelength is rarely studied, unless it is a coincidental consequence of varying the prepared excited state. Therefore the possibility that photoelectrons that are emitted with different kinetic energies experience significantly different dynamics cannot be excluded, but has usually been assumed to be unlikely. In this Letter we show that in the well-studied molecule paradifluorobenzene this optimism is misplaced.

Resonances in valence photoionization are well known in synchrotron studies of gas phase molecules in which the energy of the single photon required to ionize can be systematically varied and photoionization cross sections, photoelectron spectra, or photoelectron angular distributions (PADs) measured. However, these studies have rarely probed the region just above threshold. In recent years shape resonances in a number of diatomic molecules as well as polyatomic molecules such as  $\text{CS}_2$  [8],  $\text{SiF}_4$  [9], and benzene [10] have been observed by this means. The photoelectron-photoion coincidence (PEPICO) method has also been used to study resonance behavior by exploiting its sensitivity to a molecular frame PAD in dissociative ionization processes [11,12]. At a resonance this molecular frame PAD shows dramatic changes as a consequence of the well-known changes in the phase shifts of the contributing radial dipole matrix elements [13]. The evidence of resonance effects in laser photoionization experiments has generally been limited to the

observation of anomalous behavior, such as non-Franck-Condon ion vibrational distributions [14], at a particular ionizing wavelength. In these studies PADs have rarely been used as a signature of a resonance, with the notable exception of some work on  $\text{O}_2$  over ten years ago [15], for which *ab initio* calculations were able to reproduce the experimental observations [16].

Paradifluorobenzene (PDFB) has been well studied by spectroscopists [17] and those interested in intramolecular dynamics [18] because as well as having a relatively large number of internal degrees of freedom it has an easily accessible first excited state and a low ionization potential. For this reason, many studies have employed multiphoton ionization to study its spectroscopy and dynamics [2,19–21], as well as those of its van der Waals complexes [22]. It is therefore important to understand the photoionization dynamics of PDFB, particularly out of its  $S_1$  (valence) electronic state in which a  $\pi$  electron is ejected. In our previous studies of this molecule we have found some puzzling results. Although the PADs observed following excitation of the  $3^15^1$  vibrational level in  $S_1$  ( $\sim 2000\text{ cm}^{-1}$  above the origin) and ionization at the excitation wavelength showed a sensitivity to an evolving alignment of molecular axes [2], the PADs observed following excitation of the  $S_1$  origin and ionization at 244 nm showed no alignment dependence and were almost isotropic. Although the radial dipole matrix elements of a direct photoionization process are expected to have a weak dependence on the photoelectron kinetic energy, this observed effect was too strong to be accounted for in this way. The origin excitation is fortuitously unique in that a second photon at the excitation wavelength does not give sufficient energy to ionize the molecule. For this reason it was decided to undertake a systematic study of the PADs that result from the excitation of the  $S_1$  origin (fixed excitation wavelength) as a function of ionization wavelength and in this article we present the results of this study. These show conclusively that the PADs have a strong dependence on ionization

wavelength over the full  $\sim 1$  eV energy range studied. In addition, the PADs show almost no dependence on the prepared alignment of the molecules prior to ionization, as demonstrated by the use of different experimental polarization geometries.

Room temperature paradifluorobenzene was seeded in helium and expanded through a pulsed nozzle into a skimmed molecular beam chamber. The skimmed molecular beam was intersected by two counterpropagating laser beams at one end of a 24 cm long, doubly mu-metal shielded drift tube. All surfaces on the inside of the drift tube were coated with graphite to minimize the buildup of contact potentials and provide an almost completely field-free environment. Photoelectrons ejected along the axis of the flight tube were detected with a 2.5 cm diameter triple microchannel plate detector mounted at the other end. The photoelectron signal was passed through an amplifier and the flight times of the photoelectrons recorded with a time-to-digital converter, which has a time resolution of 1 ns.

The excitation laser was a pulsed Nd:YAG pumped dye laser, the output of which was doubled and then mixed with the Nd:YAG fundamental to producing light at 271 nm which is resonant with the  $S_1 \leftarrow S_0$  origin band in PDFB. The frequency doubled output of a second Nd:YAG pumped dye laser was used to produce the required wavelengths to ionize the excited molecules. The energy of two photons at 271 nm (9.13 eV) is less than the PDFB ionization potential (9.16 eV) and so no one-color resonant ionization occurs. The second photon wavelength was chosen to be off resonance with any  $S_1 \leftarrow S_0$  transitions and varied in the range 266 to 225 nm. A small background signal was detected only at the shorter ionizing wavelengths and was largely due to photoemission of electrons from surfaces within the vacuum chamber with a very small contribution from single color nonresonant ionization. Thus, we observed a relatively clean two-color signal and there was no need for a background subtraction.

Each laser beam was passed through a zero-order half wave plate before crossing the molecular beam. The wave plates were rotated by a computer controlled stepper motor, enabling  $\theta$ , the angle between the polarization vector of the ionizing light and the direction of ejection of the photoelectrons, to be varied. The angle between the polarization vectors of the synchronized excitation and ionization beams was fixed at either  $0^\circ$  or  $90^\circ$  and the polarization vectors of both beams were rotated together and with respect to the time-of-flight axis to give five angles of ejection ( $\theta = 0^\circ, 22.5^\circ, 45^\circ, 67.5^\circ,$  and  $90^\circ$ ). In order to minimize the effect of possible laser power fluctuations during the experiment, photoelectron spectra were accumulated for 1000 laser shots at each value of  $\theta$  and this process was repeated at least 40 times. In addition, care was taken to ensure that neither the excitation nor ionization steps were saturated. The photoelectron spectra were converted from their original form, as a

function of electron time of flight, to a function of internal energy of the PDFB ion.

Photoelectron spectra following the excitation of the  $S_1$  origin band at 271 nm and ionization with a series of different wavelengths are presented in Fig. 1. The spectra extend from threshold up to  $3000 \text{ cm}^{-1}$  of ion internal energy and were measured at  $\theta = 0^\circ$  with parallel excitation and ionization polarization vectors. The photoelectron spectra all show clearly resolved peaks corresponding to different vibrational levels of the PDFB ground state ion. These peaks can be unambiguously assigned by comparison with the work of Sekreta *et al.* [19], and because a number of vibrational frequencies of the PDFB ion ground state are well known [19,20]. The first six intense peaks in Fig. 1, occurring at ion internal energies of  $0 \text{ cm}^{-1}$ ,  $433 \text{ cm}^{-1}$ ,  $836 \text{ cm}^{-1}$ ,  $1147 \text{ cm}^{-1}$ ,

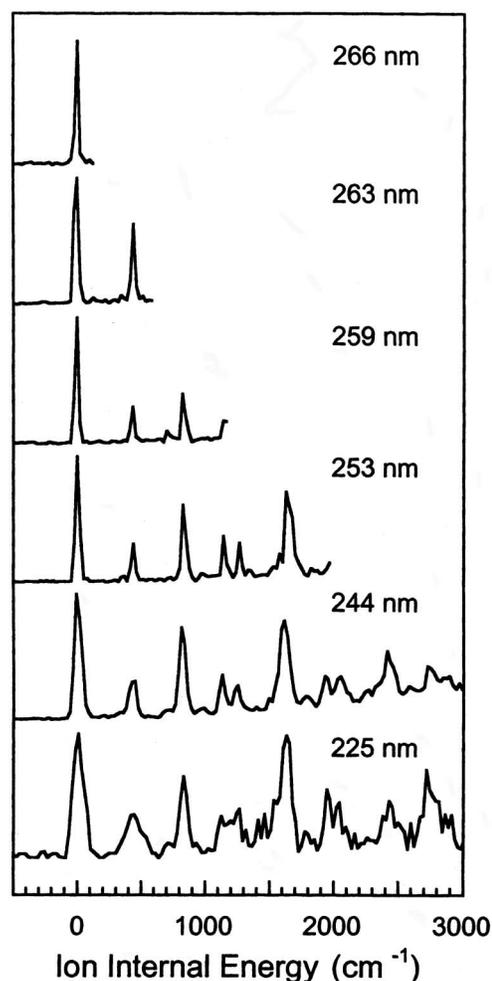


FIG. 1. Photoelectron spectra following the excitation of the  $S_1$  origin transition in PDFB at 271 nm. Six different wavelengths of ionizing light were used as labeled on each spectrum. The energy in excess of the PDFB ionization potential corresponding to the actual wavelengths used is  $446 \text{ cm}^{-1}$  (108 meV),  $1463 \text{ cm}^{-1}$  (285 meV),  $3950 \text{ cm}^{-1}$  (919 meV), respectively. Each spectrum has been scaled so that the peak corresponding to the ground vibrational state of the ion has the same intensity.

1260  $\text{cm}^{-1}$ , and 1644  $\text{cm}^{-1}$ , correspond to the ion vibrational states  $0^0$ ,  $6^1$ ,  $5^1$ ,  $4^1$ ,  $5^1 6^1$ , and  $2^1$ , respectively, where the modes are labeled using Mulliken notation [23]. Although the resolution and signal-to-noise ratio deteriorate slightly as the ionizing energy is increased, the  $0^0$  peak is clearly resolved at all wavelengths and is significantly more intense than any background contribution. The straightforward assignment of these spectra allows us to rule out the contribution of processes such as fragmentation or ionization from higher electronic states to our data.

In Fig. 2 we show polar plots of photoelectron intensity corresponding to the  $0^0$  ion vibrational state only. We have chosen to present this data for a single resolved state so that the total photon energy corresponds to a single photoelectron kinetic energy (see later). The data were fitted to the function  $I(\theta, \phi) = \sum_L \beta_{L0} Y_{L0}(\theta, \phi)$ , where  $L = 0, 2, 4$  and  $Y_{L0}(\theta, \phi)$  are spherical harmonics. The  $\beta_{20}$  and  $\beta_{40}$  values were normalized by dividing by  $\beta_{00}$  and the normalized  $\beta_{L0}$  values from the fits used to produce the plots of fitted photoelectron intensity (solid line), which overlay the normalized experimental data (points with error bars). The PADs observed for the perpendicular polarization geometry (not shown) are almost identical. Qualitatively, it can be seen that whereas at 266 nm the PAD is strongly peaked at  $0^\circ$  and  $180^\circ$ , as the ionizing wavelength is decreased from 263 to 253 nm the PADs become increasingly less peaked in this direction, becoming almost isotropic at 244 nm and peaked at  $90^\circ$  and  $270^\circ$  at 225 nm. Thus there is a dramatic change in the shape of the PAD for this single ion vibrational state as a function of ionizing wavelength, or alternatively as a function of photoelectron kinetic energy. Inspection of our data for the higher ion vibrational states reveals that

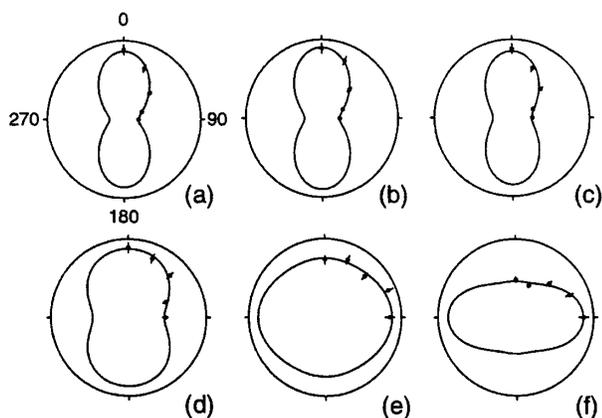


FIG. 2. Polar plots of photoelectron intensity as a function of ejection angle for the vibrational ground state of the ion. The distributions were measured with parallel excitation and ionization polarizations at six ionization wavelengths as in Fig. 1, (a) 266 nm, (b) 263 nm, (c) 259 nm, (d) 253 nm, (e) 244 nm, and (f) 225 nm. The experimental data are shown as points with error bars. The solid line is a fit to the function  $I(\theta, \phi) = \sum_L \beta_{L0} Y_{L0}(\theta, 0)$ , where  $L = 0, 2, 4$ .

PADs for different ion vibrational states at the same photon energy have different shapes.

The behavior of the PADs in Fig. 2 can be quantified by examining the  $\beta_{20}$  and  $\beta_{40}$  values resulting from the fit. A plot of the normalized  $\beta_{20}$  and  $\beta_{40}$  parameters as a function of electron energy for the  $0^0$  ion vibrational state is presented in Fig. 3. The  $\beta_{40}$  values are small and close to zero at all wavelengths suggesting a lack of sensitivity to any prepared alignment in the intermediate state. This is borne out by the absence of changes observed in the PADs measured in the perpendicular polarization geometry. We also note that similar PADs have been observed in experiments in which overlapped picosecond laser pulses have been used to excite and ionize PDFB [24] indicating that it is not rotational averaging that gives rise to the lack of alignment sensitivity. The change in anisotropy with increasing ionization energy is therefore solely due to a decrease in the  $\beta_{20}$  values which change dramatically from 0.5 at a photoelectron kinetic energy of  $\sim 446 \text{ cm}^{-1}$  ( $\sim 55 \text{ meV}$ ) to  $-0.21$  at a photoelectron kinetic energy of  $\sim 7411 \text{ cm}^{-1}$  (919 meV).

Because the energy of the first photon is fixed and thus the initial state does not change, the most likely explanation for the observed behavior is a resonance in the continuum. Possibilities for this are autoionization, a Cooper minimum, or a shape resonance, all of which have been invoked as being responsible for dramatic variations in PADs as a function of ionizing energy [10,25,26]. Because the energy range over which our PADs are observed to change is large and there is every reason to believe that we have not probed the total range we discount autoionization as being the mechanism involved as a consequence of the sharp structure usually associated with such processes. Although Cooper minima

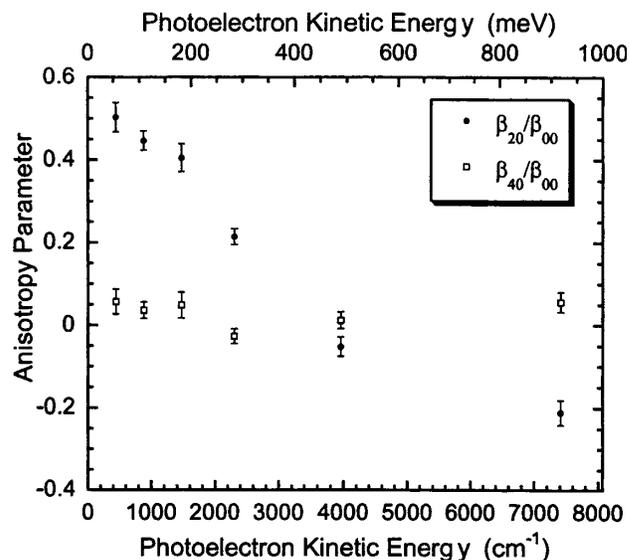


FIG. 3. The normalized  $\beta_{20}$  and  $\beta_{40}$  parameters taken from the fit shown in Fig. 2 as a function of photoelectron kinetic energy.

have been invoked in chlorobenzene [25], bromobenzene [27], and iodobenzene [28] this effect involves ejection of a lone pair electron and is far above threshold. A lower energy Cooper minimum has been observed following ionization of an excited state in OH [29], but the arguments in its support involve the ionization of Rydberg states in small molecules. Therefore we propose the presence of a shape resonance near threshold in PDFB. A shape resonance has been observed and calculated fairly near to threshold in the one-photon ionization of benzene [10,30,31], and it has been suggested that chlorobenzene has similar behavior [25].

The observation of such an effect in a molecule such as PDFB suggests that experiments in which PADs from excited state polyatomic molecules are measured as a route to intramolecular dynamical information need to be carefully considered. In experiments in which the total photon energy is not varied, in which vibrational states are resolved before and after ionization, and in which the effects of a time delay between excitation and ionization are studied will indeed contain important information on intramolecular dynamics. However, experiments in which ion vibrational states are unresolved may well give rise to PADs that are misleading, particularly as a number of different ion vibrational states are typically formed following the ionization of a valence state in a polyatomic molecule. The lack of alignment sensitivity observed in this work is also significant for dynamics experiments in which  $\pi$  electrons are photoejected from aromatic rings. Our results also demonstrate that great care needs to be taken in the determination of the phase shifts of the radial dipole matrix elements used in calculations, and in making qualitative arguments relating the shape of PADs to the electronic symmetry or alignment of an ionized intermediate state.

In conclusion, we attribute the strong variation of the observed PADs from  $S_1$  PDFB as a function of photoelectron kinetic energy to a shape resonance in the continuum. We caution experimentalists, particularly those who are using femtosecond time-resolved PADs as a probe of intramolecular dynamics, to consider the possibility that significantly different PADs may be associated with each unresolved ion vibrational state formed.

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