



# A demonstration of the Franck–Condon principle upon ionization

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## Abstract

Vibrationally resolved ionization probabilities have been recorded for laser-desorbed jet-cooled diphenylamine via the mass analyzed threshold ionization (MATI) technique. The observed MATI spectra from selected laser-prepared vibrational levels in the first electronically excited singlet state of DPA are a clear demonstration of the Franck–Condon principle upon ionization. The shape of the vibrational wavefunction in the intermediate electronic state is seen directly reflected in the spectra.

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## 1. Introduction

According to the Franck–Condon principle, the relative intensities of vibrational transitions in molecules are determined by the overlap integral of the vibrational wavefunctions of the levels coupled in the transition. For an instructive demonstration of this principle, a large geometrical change of the molecule along a well-defined normal-coordinate must occur in the transition and vibrationally resolved transition intensities must be recorded. The torsion angle of the phenyl rings in the diphenylamine (DPA) molecule provides a normal-coordinate along which such a change occurs upon ionization. Vibrationally resolved ionization probabilities can be recorded via the mass analyzed threshold ionization (MATI) technique [1]. In this Letter, we report the experimental MATI spectra from selected laser prepared torsional levels in the first electronically excited singlet state of DPA. These MATI spectra are a clear

demonstration of the Franck–Condon principle upon ionization; the shape of the torsional wavefunction in the intermediate electronic state is seen directly reflected in the spectra.

## 2. Experimental

The experiments are performed in a laser desorption jet-cooling molecular beam spectrometer. In this spectrometer diphenylamine (DPA) is desorbed with a laser pulse from a sample substrate that is positioned close to the orifice of a pulsed jet expansion. A frequency-doubled Nd:YAG laser with a  $10^7$  W/cm<sup>2</sup> fluence is used for desorbing the DPA from a piece of activated carbon that acts as a matrix and that can contain a large buffer quantity of DPA. The pulsed valve is operated with a 2 bar Ar backing pressure and delivers 20  $\mu$ s duration gas pulses at a repetition rate of 10 Hz. The laser-desorbed molecules are entrained in the argon jet and their internal energy is efficiently cooled by multiple collisions in the expansion region; ro-vibrational temperatures comparable to temperatures obtained in ‘conventional’ molecular beam seeding experiments are obtained with this

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laser desorption approach [2]. Laser excitation of DPA to the first electronically excited singlet state is performed with a frequency-doubled pulsed tunable dye laser in the 309–305 nm region via the  $S_1 \leftarrow S_0$  transition. In the electronic excitation spectrum of jet-cooled DPA a long progression in the low-frequency phenyl-ring torsion mode with a  $62.5 \text{ cm}^{-1}$  frequency in the  $S_1$  state is observed [2]. In the experiments reported here selected torsional levels in the  $S_1$  state of DPA are prepared with the dye laser. A second frequency-doubled dye laser is used for subsequent ionization of the DPA molecules, and parent cations are mass-selectively detected in a linear time-of-flight setup of the configuration as described by Wiley and McLaren [3].

To accurately determine the vibrationally state-resolved ionization probabilities out of selected torsional levels in the  $S_1$  state we performed mass analyzed threshold ionization spectroscopy (MATI) [1]. MATI takes advantage of the field ionization of long-lived high Rydberg states of the neutral molecules to signal an ionization threshold. A variety of experimental approaches to enable selective detection of these long-lived high Rydberg states have been demonstrated [1,4–7]. We applied MATI in our linear TOF setup according to the scheme depicted in Fig. 1. The (unfocused) excitation and ionization laser beams have a 1.5 mm beam diameter and are spatially overlapped, intersecting the molecular beam midway between the extraction plates of our mass spectrometer. As the lifetime of the  $S_1$  state is of the order of a nanosecond a good temporal overlap of the  $\approx 5 \text{ ns}$  pulses is also crucial. If the ionization laser is scanned over the ionization onset and further into the ionization continuum both direct ions and highly excited Rydberg neutrals, belonging to series that converge to bound levels in the ion, are produced when the wavelength is right, i.e. when the total energy used for ionization is close to the energy of a bound level in the ion. With a bias field of  $2 \text{ V/cm}$  in the extraction region the directly produced ions, the so-called prompt ions, are spatially separated from the Rydberg neutrals. This field will ionize a known subset of Rydberg levels, namely those that are within  $k\sqrt{E} \text{ (V/cm)}$  of the actual field-free ionization potential, where the constant  $k$  is between the diabatic and adiabatic limiting values of 4 and  $6 \text{ cm}^{-1}$ , respectively [8,9]. The bias field thus forms the high-

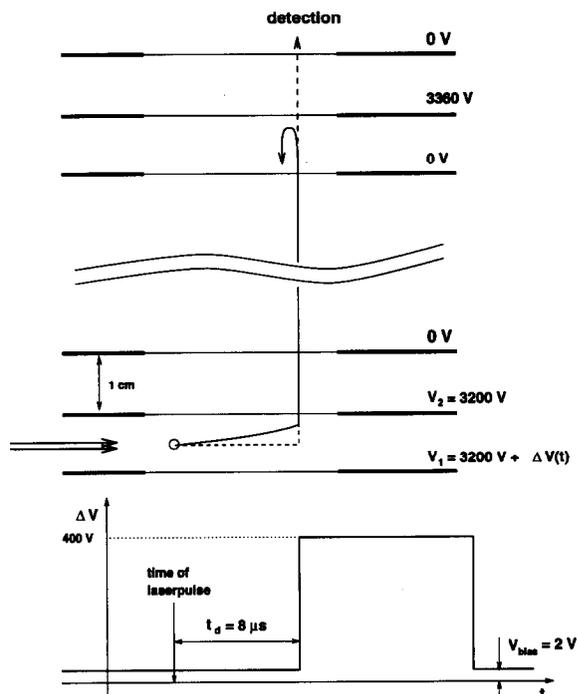


Fig. 1. Schematic representation of the ion-optics and the time-dependent extraction fields used to make background-free detection of the field-ionized Rydberg neutrals possible. Ions as well as Rydberg neutrals are produced between the extraction plates of a linear time-of-flight spectrometer at the position indicated by the circle. After a time-delay of  $8 \mu\text{s}$  an extraction pulse is applied to field ionize the Rydberg neutrals and to accelerate the ions toward the detector. Both the trajectories of the prompt ions (solid curve) and of the (field-ionized) Rydberg neutrals (dashed curve) are indicated. The static ion reflector makes background-free detection of the MATI ions possible.

frequency cutoff of the observed Rydberg series.

After a time delay of  $8 \mu\text{s}$  the highly excited Rydberg neutrals are field ionized by a field of  $400 \text{ V/cm}$  and together with the prompt ions they are accelerated toward the ion detector, placed  $60 \text{ cm}$  further. The time delay is used to get sufficient spatial separation of the Rydberg neutrals and the prompt ions with moderate bias fields. In addition, the time delay determines the low-frequency cutoff of the observed series of the Rydberg neutrals; the lifetime of the Rydberg levels increases with increasing values of the principal quantum number  $n$ , and low Rydberg levels will not survive this time delay. The experimental geometry prevented us from using even longer delay times due to the escape of prompt ions and Rydberg

neutrals from the ion-extraction region. There have been discussions in the literature on the actual scaling of the lifetimes of the high Rydberg states with the  $n, l$  quantum numbers [10] and it has been experimentally demonstrated that the lifetimes of the high-lying Rydberg states are determined not only by intramolecular non-radiative processes but also by intermolecular Rydberg-ion or Rydberg-Rydberg interactions [11]. In the experiments reported here the total ion density in the extraction region was kept below  $10^5$  ions/cm<sup>3</sup> and a substantial amount of highly excited Rydberg neutral molecules survived the 8  $\mu$ s delay time under these experimental conditions.

The spatial separation of the prompt ions and the Rydberg neutral molecules results in a difference in potential energy of both groups of ions after the pulsed extraction field is switched on. This energy difference is used to discriminate against the unwanted prompt ions by applying the proper voltage to the ion reflector, placed just in front of the ion detector, as schematically indicated in Fig. 1. Thus, background free detection of the field-ionized Rydberg neutrals is possible and the vibrationally resolved ionization probabilities can be measured.

### 3. Results and discussion

The resulting MATI spectra of selected torsional levels in the  $S_1$  state of DPA are shown in Fig. 2. The frequency scale underneath the spectrum is the total (two-color) two-photon energy used in the excitation process from the vibrationless level of neutral DPA in its electronic ground state. The three different MATI spectra are recorded via the  $v' = 0, 1$  and 2 levels of the torsion-vibration in the electronically excited  $S_1$  state of DPA, as indicated in the figure. The quantum numbers of the torsion-vibration in the ion to which the observed Rydberg series are converging are indicated in the upper part of the figure. The vertical dashed line indicates the position of the field-free adiabatic ionization potential (IP) of DPA at  $58600 \pm 5$  cm<sup>-1</sup>. The individual MATI peaks are  $\approx 10$  cm<sup>-1</sup> wide and comprise Rydberg levels in the  $n = 50-150$  part of the series. The different cutoff mechanisms for the high and low Rydberg levels discussed before lead to the observed asymmetric line-shape. The sharpness of the cutoff at the high-energy

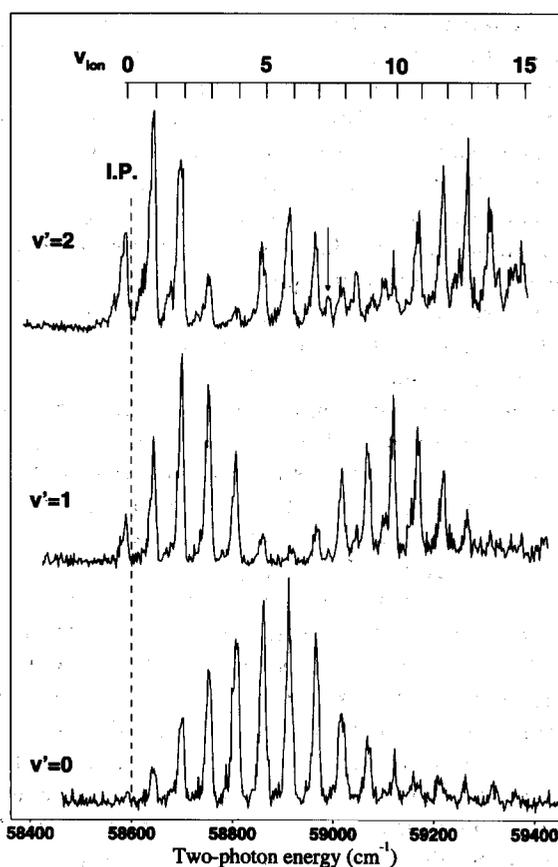


Fig. 2. MATI spectra recorded via the three lowest torsional levels in the first electronically excited singlet state of diphenylamine. The torsional frequency in the DPA cation is  $53$  cm<sup>-1</sup>. The probability distribution for the torsional angle of the phenyl rings in the various laser prepared torsional levels in the  $S_1$  state is directly reflected in the envelope of the MATI peak intensities. The total energy needed for ionization of DPA from the vibrationless level in the ground state of the neutral molecule is  $58600 \pm 5$  cm<sup>-1</sup>.

side is smeared out by the residual internal energy of the jet-cooled DPA molecules.

From the MATI spectra shown in Fig. 2 it is deduced that the torsional mode in the ground state of the ion has a frequency of  $53$  cm<sup>-1</sup> and that the torsional potential is well described in a harmonic model. Although we are dealing with a large molecule, it is evident from the spectra that it represents a clean model system in which the geometrical change upon ionization is predominantly along one well-defined normal coordinate, the torsional angle. There is a slight activity in a mode around  $400$  cm<sup>-1</sup>, indicated by a vertical arrow in the upper spectrum of Fig. 2,

and a torsional progression is build on this mode as well. Although this  $400\text{ cm}^{-1}$  mode is present in all three spectra it is especially evident in the MATI spectrum starting from the  $v' = 2$  level as here it coincides with the second minimum in the overall intensity distribution of the MATI spectrum.

The intensity distribution in the three spectra is quantitatively reproduced in a harmonic oscillator model when a shift in equilibrium position is taken that corresponds to a change of  $22^\circ$  in the summed dihedral angles of the phenyl rings upon ionization from the  $S_1$  state. It is to be expected that DPA changes from a pyramidal geometry around the N nucleus in the ground state of the neutral molecule toward a (more) planar structure in the ground state of the ion. This releases the steric hindrance of the phenyl rings somewhat, allowing for a more optimum conjugation of the phenyl rings.

The shape of the torsional wavefunction in the  $S_1$  state is seen directly reflected in the MATI spectra of DPA as can be understood from the following. For high vibrational quantum numbers the vibrational probability distribution is peaked near the walls of the potential. Therefore, the overlap integral of this high vibrational level in the ground state of the ion with a vibrational level in the  $S_1$  state is a measure of the probability density in the lower potential at the position where the upper level probability is peaked. Thus, scanning over different vibrational levels in the ion (the upper potential) is mapping the square of the wavefunction in the  $S_1$  state of the neutral molecule (the lower potential) along the relevant coordinate, in this case along the torsional angle. All three MATI spectra show the peaks and nodes in the respective wavefunctions at the expected positions. Fig. 2 thereby forms a textbook example of the Franck–Condon principle upon ionization.

In conclusion, we have observed that the vibrational intensity distribution upon ionization of the molecule diphenylamine is correctly described in the

Franck–Condon picture. The Franck–Condon principle is based on the Born–Oppenheimer approximation, i.e. the assumption that the nuclear motion is frozen on the time scale of the movement of the electron. The data presented here explicitly show that the Franck–Condon description of vibrational transition intensities even holds for excitation to highly excited Rydberg states of the neutral molecule, something that is not a priori evident as these Rydberg states are no longer correctly described in the Born–Oppenheimer approximation.

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