

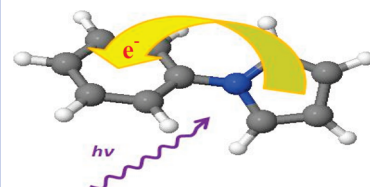
# Stark-Effect Studies of 1-Phenylpyrrole in the Gas Phase. Dipole Reversal upon Electronic Excitation

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**ABSTRACT** High-resolution fluorescence excitation experiments on 1-phenylpyrrole in a molecular beam, both in the absence and presence of an applied electric field, show that the electronic state responsible for the strong features in the gas-phase UV absorption spectrum is the  $^1L_b$  state, that this state is significantly more planar than the ground state, and that the direction of the permanent electric dipole moment in the  $^1L_b$  state is reversed relative to that of the ground state. Implications of these findings for intramolecular charge transfer in the isolated molecule are discussed.

**SECTION** Dynamics, Clusters, Excited States



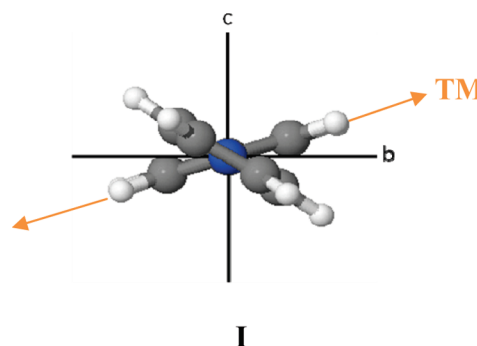
The molecule 1-phenylpyrrole (1PP) has attracted much attention since it was discovered in 1983 that it exhibits a long wavelength shoulder in its fluorescence spectrum in acetonitrile.<sup>1</sup> Originally, it was thought that electronic excitation led to the formation of a twisted intramolecular charge-transfer (TICT) state which might be stabilized in a polar solvent.<sup>2</sup> Later, it was shown in a supersonic jet study of 1PP<sup>3</sup> that the electronically excited  $S_1$  state, though twisted, is more planar than the ground electronic state. However, Proppe et al.<sup>4</sup> have argued on the basis of a theoretical study of TICT in 1PP that the transition studied by Okuyama et al.<sup>5</sup> may not correspond “to the electronic transition responsible for the spectroscopic feature with maximum intensity in the lowest-energy region of the absorption spectrum”, thereby creating some doubt about the relevance of the gas-phase results.

Photoinduced ICT states of organic compounds play a fundamental role in many processes of current interest.<sup>5</sup> For this reason, we report here the results of a high-resolution laser study of 1PP in a molecular beam, both in the absence and presence of a static electric field. These results show that the state responsible for the strong feature in the absorption spectrum is the  $^1L_b$  state, that this state is significantly more planar than the ground electronic state, and that the direction of the permanent electric dipole moment in this state is reversed relative to that in the ground electronic state. Reversal of the dipole direction may play a previously unappreciated role in the CT process in many molecules.

Detailed descriptions of our experimental methods are given in the Supporting Information. There, we also present the results of both vibrationally and rotationally resolved experiments on 1PP in the absence of an electric field. The vibrationally resolved fluorescence excitation spectrum is virtually identical to that presented by Okuyama et al.;<sup>3</sup> the first 1000  $\text{cm}^{-1}$  are dominated by a long progression of bands spaced by intervals of  $\sim 50 \text{ cm}^{-1}$ . Rotationally resolved spectra of three of these bands at  $+269.0$ ,  $+316.9$ , and  $+364.5 \text{ cm}^{-1}$  with respect to the weak origin band (originally assigned as  $T_0^8$ ,  $T_1^9$ , and  $T_0^{10}$ , where T represents a ring-torsional mode<sup>3</sup>) show that all transitions originate in the same ground-state vibrational level, that the upper-state vibrational levels reached in the three transitions

all have inertial defects that are substantially lower (in magnitude) than those of the ground state, and that the PES along the torsional coordinate in the excited state most likely has a greatly reduced barrier to planarity and a greatly increased barrier to perpendicularity compared to the ground state.

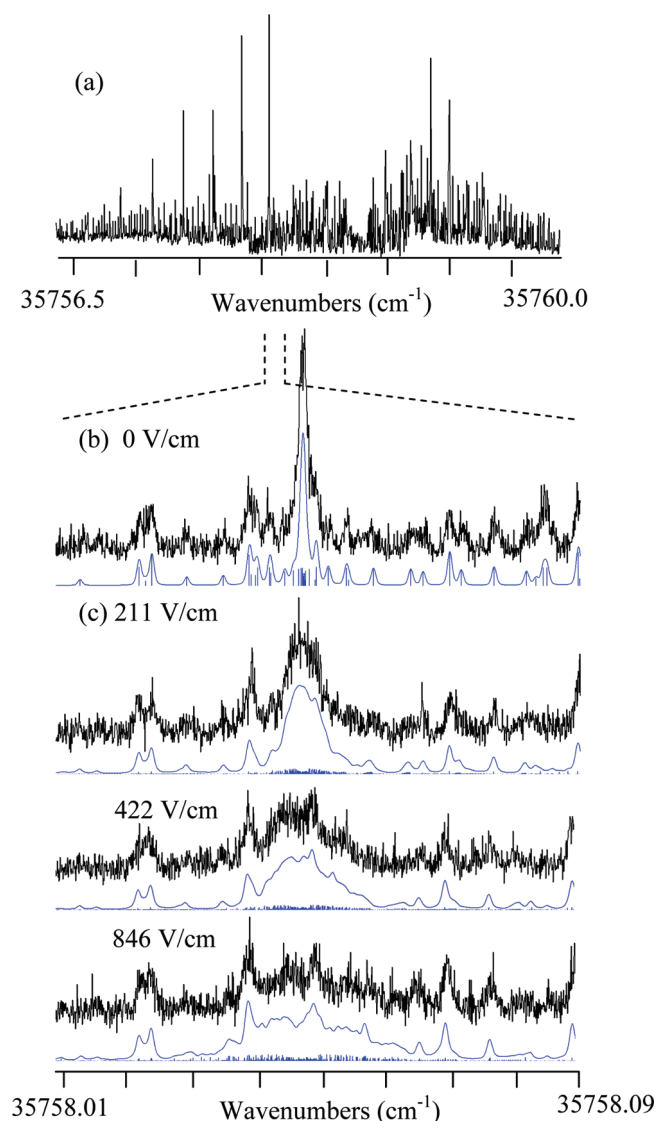
Also relevant to the issue of CT in the electronically excited state of 1PP is the behavior of the electronic spectrum in the presence of an electric field. Figure 1 shows an example, the high-resolution spectrum of the  $0_0^0 + 269 \text{ cm}^{-1}$  band at zero field, and selected portions of this spectrum at Stark fields of 211, 423, and 846 V/cm. Like the other bands examined at high resolution, this band is a hybrid band consisting of 87.5% b-type character and 12.5% c-type character. No a-type character is observed. This shows that the state accessed in these experiments is a  $^1L_b$  state (in the language of Proppe et al.<sup>4</sup>, the  $1^1B$  state, comprised principally of two one-electron excitations, 42.6% HOMO–1 to LUMO+1 and 26.7% HOMO–2 to LUMO). Excitation of this state utilizes a transition moment that is perpendicular to the long axis of the molecule, lying in the plane of the benzene ring, and rotated by  $21^\circ$  around the  $a$ -axis of 1PP (see I).



The electric field tuning behavior of a specific transition in an electronic spectrum depends on the values of all three

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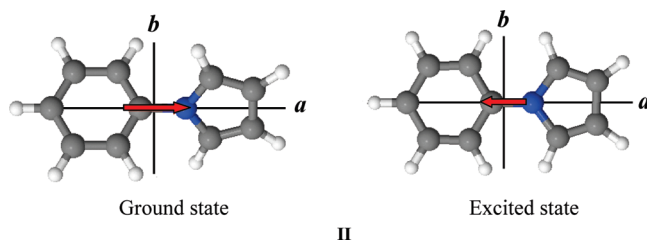
**Figure 1.** (a) Rotationally resolved spectrum of the  $0_0^0 + 269\text{ cm}^{-1}$  band of 1-phenylpyrrole in the zero field. (b) A portion of the Q-branch from the zero-field spectrum shown at full resolution. The most intense transitions are  $[(J', K_a', K_c') \leftarrow (J'', K_a'', K_c'')] [(10, 3, 8) \leftarrow (10, 4, 7), (11, 3, 9) \leftarrow (11, 4, 8), \text{ and } (9, 3, 7) \leftarrow (9, 4, 6)]$ . The simulated spectrum is shown both as discrete transitions and as a contour comprised of 30 MHz Gaussian and 13 MHz Lorentzian contributions to the observed Voigt line shape profiles. (c) Corresponding portions of the spectrum collected in the presence of the indicated electric fields.

permanent dipole moment components in both electronic states. As in microwave spectroscopy,<sup>6</sup>  $\mu_a$  connects states having  $\Delta K_a = 0, \pm 2, \dots$  and  $\Delta K_c = \pm 1, \pm 3, \dots$ ;  $\mu_b$  connects states having  $\Delta K_a = \pm 1, \pm 3, \dots$  and  $\Delta K_c = \pm 1, \pm 3, \dots$ ; and  $\mu_c$  connects states having  $\Delta K_a = \pm 1, \pm 3, \dots$  and  $\Delta K_c = 0, \pm 2, \dots$ . The sensitivity of the UV experiment to the different dipole components also depends on the orientation of the transition dipole;<sup>7</sup> for a b-type transition, the Stark effect is linear for levels connected by  $\mu_a$  and  $\mu_c$  and quadratic for levels connected by  $\mu_b$ . This is apparent from Figure 1; the b-type Q-branch lines with  $\Delta K_a$  and  $\Delta K_c = \pm 1$  are split more than others.

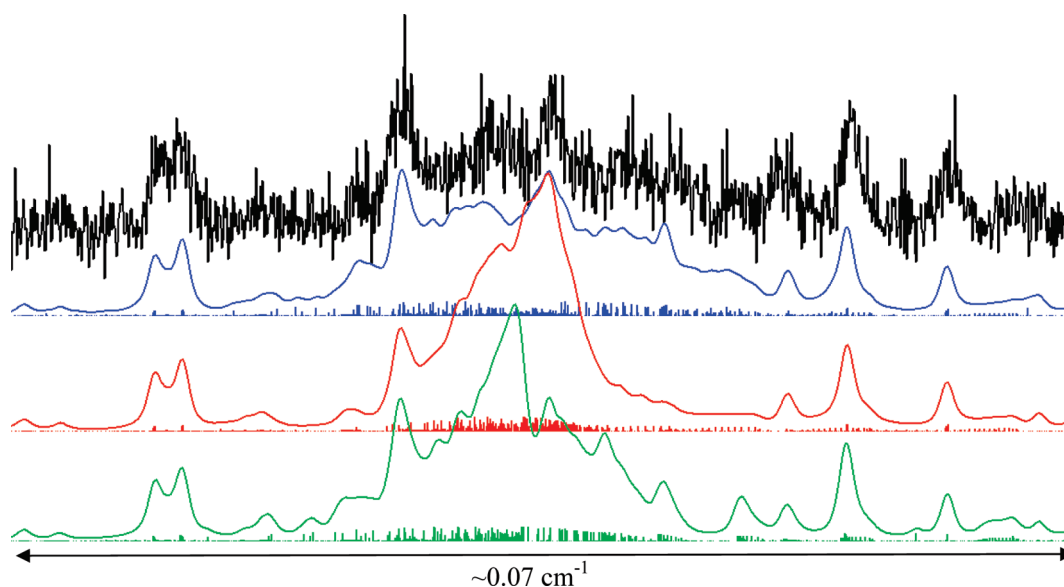
A least-squares fit of this behavior yields the values  $\mu_a(S_0) = \pm 1.56 \pm 0.01\text{ D}$  and  $\mu_a(S_1) = \mp 0.94 \pm 0.01\text{ D}$ . As expected, both  $\mu_b$  and  $\mu_c$  were found to be zero in both electronic states, to within  $\pm 0.01\text{ D}$ . Our fits of the spectra shown in Figure 1 included 64 lines and yielded an OMC standard deviation of 4.86 MHz, small compared to the observed line width of 40 MHz.

Substantial charge reorganization is revealed by the measured values of  $\mu_a$ ;  $|\Delta\mu_a| \approx 2.5\text{ D}$  upon excitation of 1PP by light. More dramatic is the change of sign. As is well-known, the absolute signs (i.e., directions) of dipole moments cannot be determined without interpretation by chemical intuition or theoretical calculations. However, our results show that the pattern of splitting with the dipole moments oriented in different directions in the two states is inherently different from that with the dipole moments pointing in the same direction. This is illustrated in Figure 2. Significantly, the spectrum also cannot be fit with an excited-state dipole moment that increases in magnitude by  $\sim 2.5\text{ D}$ .

Previous estimates of the ground-state dipole moment of 1PP include a measured value of  $|1.39|\text{ D}$  (in benzene solution at  $30\text{ }^\circ\text{C}$ )<sup>8</sup> and calculated values (for a twisted structure) of  $-1.51$ ,<sup>5</sup>  $-1.3$ ,<sup>9</sup> and  $-1.9\text{ D}$ .<sup>10</sup> The negative sign of the dipole of ground-state 1PP indicates that the center of negative charge is located on the pyrrole ring, which agrees with chemical intuition (see II). Thus, our measured dipole moment for the ground state can be assigned the value  $-1.56\text{ D}$ , and our measured dipole moment for the excited state can be assigned the value  $+0.94\text{ D}$ . The center of the negative charge in the excited state is located on the benzene ring. Proppe et al.<sup>4</sup> predict the electronically excited state values of  $-1.00\text{ D}$  for the twisted  $1^1\text{B}$  state and  $+3.10$  for the twisted  $2^1\text{A}$  state, a conclusion with which Haas and co-workers<sup>9,10</sup> qualitatively concur. Additionally, Yoshihara et al.<sup>11</sup> have determined from a careful solvatochromatic study that the excited-state dipole of 1PP could either be negative or positive,  $-3.0$  or  $1.6\text{ D}$  (relative to an assumed value of  $10\text{ D}$  for the LE state of DMABN).



A dipole change of  $\Delta\mu \approx 2.5\text{ D}$  is calculated to result from a transfer of charge of  $\sim 0.15\text{ e}^-$  from the pyrrole ring to the benzene ring, whose centers of mass are separated by  $3.6\text{ \AA}$ . This amount of charge transfer could easily explain the magnitude of the measured red shift in solution. Notwithstanding the possible effects of solvent, we estimate for the gas-phase molecule a red shift of  $700\text{ cm}^{-1}$ . More problematic is the nature of the  $S_1$  state accessed in our experiments. According to Proppe et al.,<sup>4</sup> the lower  $1^1\text{B}$  state has very low oscillator strength and a negative dipole moment, whereas the higher lying  $2^1\text{A}$ ,  $2^1\text{B}$ , and  $3^1\text{A}$  states have both higher oscillator strengths and positive dipole moments. Thus, it may



**Figure 2.** Portions of the 846 V/cm spectrum fit with  $\mu_a'' = -1.56$  D and  $\mu_a' = 0.94$  D (top, blue);  $\mu_a'' = -1.56$  D and  $\mu_a' = -0.94$  D (middle, red); and  $\mu_a'' = -1.56$  D and  $\mu_a' = -4.06$  D (bottom, green).

be that the state whose properties are measured here is a mixed state, containing both locally excited as well as charge-transfer character. Such mixing may result from efficient vibronic coupling involving the more polar  $^1L_a$  state, as in the original PICT model for charge transfer in electronically excited states.<sup>12</sup>

**SUPPORTING INFORMATION AVAILABLE** Information regarding methods and additional spectroscopic results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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