Stark Shift of Rotational Lines in the UV Spectrum of the Charge-Transfer Molecule Benzonitrile†

Klaus Siglow and Hans Jürgen Neusser*

Institut für Physikalische und Theoretische Chemie, Technische Universität München,
Lichtenbergstr. 4, 85748 Garching, Germany

Received: April 17, 2001; In Final Form: June 4, 2001

We present the resolved Stark splitting of rovibronic lines in the resonance enhanced multiphoton ionization spectrum of benzonitrile caused by an electric field up to 700 V/cm. The Stark spectrum is theoretically reproduced yielding a value of 4.5(1) Debye for the dipole moment of the excited S_1 state. The same value is found from the Stark splitting of the 11_0^1 band at an excess energy of 703 cm^{-1}. The slight increase of the dipole moment compared to the ground-state value of 4.18 D and the absence of local perturbations in the spectra demonstrate that there is no detectable influence of the theoretically predicted charge-transfer state caused by a rehybridization of the carbon atom in the cyano group. Our results further show that the presence of electric fields during excitation can lead to a broadening of REMPI spectra and should be avoided in rotational resolution work on polar molecules.

I. Introduction

Charge-transfer states in organic molecules with a large dipole moment are a matter of current interest. They are expected to act sensitive to the local environment and cause a red-shifted fluorescence in polar solvents. Benzonitrile (BN) and some of its derivatives are prototype systems for intramolecular charge-transfer processes. In their initial experiments Lippert et al.[1] detected a dual fluorescence of 4-dimethylaminobenzonitrile (DMABN) in polar solvents which was finally attributed to the emission from a charge-transfer state coupled to the local S_1 state. From an experimental study of different sterically hindered *o*-CH_3-derivatives of DMABN, Grabowski et al. concluded the existence of an energetically favored state involving a twist of the methyl group (twisted intramolecular charge-transfer: TICT).[2,3] In the meantime, two alternative mechanisms were proposed to explain the experimental findings: the planarity induced charge-transfer model (PICT)[4] and the model of rehybridization by intramolecular charge-transfer (RICT).[5] The latter model predicts a rehybridization of the carbon atom in the cyano group from *sp* to *sp*^{2}, leading to the existence of charge-transfer states, which are therefore predicted also in the more simple systems of isolated 4-amino-BN and BN without the influence of a surrounding solvent. Mordzinski et al.[6] found dual fluorescence even in bare BN consisting of sharp features and a broad red-shifted emission at somewhat longer wavelengths than calculated by Sobolewski and Domcke[5] for a RICT process. The broad red-shifted component of the fluorescence was then resolved by Sekiya and co-workers[7] ruling out their assignment as charge-transfer states.

Microwave spectroscopy provided accurate structural data on the BN monomer[8] and several of its van der Waals clusters[9−12] in the neutral ground state. High-resolution UV spectra measured in our group added structural information on the S_1 state in BN, BN·Ar, and BN·H_2O.[10,13,14] Very recently, we obtained first results from vibrationally resolved one- and two-photon excitation to higher vibrational states of the monomer.[15] Up to now, however, no signs of contributions from charge-transfer states by coupling and mixing have been found in the investigated excess energy range of the S_1 state of BN.

One of the most direct signatures of a charge-transfer state would be a significant increase of the dipole moment in the excited state of the molecules or clusters,[16−18] as was observed in the basic works of Mulliken[19] in charge-transfer complexes and in aromatic molecules by Nagakura.[20] In its electronic ground state, BN features a large dipole moment of 4.18 D.[21] Calculations yield dipole moments of 4.23 D for the S_0 ground state of BN (A_1 in point group C_{2v}), reproducing well the experimental value.[5] The dipole moment in the postulated RICT state (A'' in point group C_s) was predicted to amount to 8.06 D, and thus a factor of 2 larger than the value of 4.2 D calculated for the nominal S_1 state (B_2 in point group C_{2v}). An early experiment by Lombardi and co-workers[22] in a gas cell at room temperature yielded a dipole moment of S_1 BN of 4.45 D measured in the vibronic band at 514 cm^{-1} excess energy. They also reported signatures of selective mixing of some rotational states of the electronic origin to a dark background state which prohibited the determination of the excited-state dipole moment in this band.[23]

In this work we present for the first time high-resolution sub-Doppler REMPI spectra of BN with and without external electric fields up to 700 V/cm. To exclude local effects and to investigate possible coupling to charge-transfer states we performed measurements of the electronic origin band 0_0^0 and the 11_0^1 band at an excess energy of 703 cm^{-1}.

II. Experimental Section

The experimental setup was described in detail elsewhere.[24] Briefly, the light of an Ar$^+$-ion laser-pumped (Coherent Innova 400) cw single-mode ring dye laser (Coherent 699/29, Rhodamine 110) is pulse amplified in three XeCl excimer laser-pumped

---

† This work is dedicated to Prof. Dr. Friedrich Dörr on occasion of his 80th birthday.

* Corresponding author. Electronic address: neusser@ch.tum.de; Fax +49 8928913412.

10.1021/jp011414x CCC: $20.00

(Lambda Physik MSC2001) amplifier stages operating with Coumarine 153 and 307 dyes. After frequency doubling UV pulses of 15 ns duration and 500 μJ energy are obtained. Their frequency width of 70 MHz is close to the Fourier transform limit. For the ionization step either a similar setup (Kr^+ ion laser-pumped cw single-mode dye laser and an amplifier chain operating with Coumarin 102 dye) or the output of a commercial broad band dye laser (Lambda Physik FL2001, Coumarin 102) is used.

For the experiments presented here, Ar as a carrier gas at a backing pressure of 3 bar was expanded supersonically through a heated reservoir (70 °C) of fluid BN and a pulsed nozzle (valve: modified Bosch automotive, orifice 200 μm diameter). Mass selective detection is realized with a home-built linear time-of-flight mass spectrometer (length of drift tube: 40 cm). The ion detector signal is integrated in appropriate time windows (Stanford Research Systems SR250 integrator) and recorded with a standard PC in a Labview environment. Relative frequency calibration is provided by a 150 MHz Fabry−Perot interferometer transmission spectrum. The absolute frequency measurement is made with a Fizeau-interferometer wave meter (ATOS LM007, absolute accuracy $\Delta\nu/\nu = 10^{-8}$) which was calibrated periodically against the output of a temperature stabilized HeNe reference laser (Sitos Messtechnik SL02/1).

For the measurements of the Stark shift, DC voltages up to 2000 V were applied to the electrodes of the ion optics of the time-of-flight mass spectrometer to provide the necessary high field strengths at the excitation region. We accepted the loss of the space focus condition in this mode of operation, as the resulting mass resolution was sufficient to selectively observe the mass peak of the BN monomer. For measurements under field-free conditions, the acceleration field in the ion optics is switched on *after* the interaction of the molecules or clusters with the laser pulses. To maintain the space focus condition in the Wiley−McLaren time-of-flight mass spectrometer in this case, positive voltages of appropriate magnitude are applied to the two electrodes surrounding the excitation region through fast semiconductor switches (rising time < 10 ns/100V) about 50 ns after laser excitation. Residual electric stray-fields in our apparatus were recently determined to be below 300 mV/cm in a experiment on Rydberg states[25] and are therefore in a range without any significance to the investigation of low electronic states in the present work.

III. Static Stark Effects in Electronic Transitions

The effect of an external electric field on the rotational spectrum of polar molecules is routinely used in microwave spectroscopy to measure the ground-state dipole moment with high precision, but only a few examples exist for electronic transitions. Lombardi and co-workers determined the excited-state dipole moments of a number of substituted benzene derivatives by rotational contour analysis (ref 22 and references therein). However, they were not able to resolve single rotational lines and their splittings in an electric field. Rotationally resolved spectra of polyatomic molecules in low electric fields were published only recently. Hese and co-workers[26] determined the polarizability of benzene from static Stark effect measurements in electric fields up to 25 kV/cm. Korter et al.[27] presented high-resolution laser induced fluorescence spectra of aniline in external electric fields and their analysis including the simulation of the Stark spectra. They found a 150% increase of the dipole moment in the excited S_1 state compared to the electronic ground state.

An extensive theoretical treatment of the Stark effect in asymmetric rotors was given by Golden and Wilson[28] and its application to UV spectra of polyatomic molecules was discussed in detail by Lombardi.[29] Different from symmetric top molecules or clusters, the Stark splitting in asymmetric tops is of second order in the field strength E, since the degeneracy in K, the projection of the total rotational angular momentum J on a molecule fixed axis, is already lifted in these systems. The asymmetric rotor usually is described in the limits of an prolate and oblate symmetric top by defining components K_a and K_c of J in these two limiting cases. However, in an external electric field K_a and K_c are no longer conserved and only the projection M of the total angular momentum J on the space fixed axis defined by the external field remains a good quantum number. If accidental degeneracies of rotational levels can be neglected, the shift of the rotational levels of an asymmetric top in an external electric field can be evaluated using second-order perturbation theory.[28] Qualitatively, the external field leads to a splitting of a $|JK_aK_c\rangle$ rotational state into sub-states with different values of M. The absolute shift of the rotational levels is thereby dominated by the value of J and is decreasing rapidly with increasing J. Even if the dipole moment and therefore the absolute splitting of a single level remains the same in both electronic states, the strong dependence of the absolute splitting on J leads to a splitting of the rovibronic transitions observed in an electronic excitation provided that $J'' \neq J' (\Delta J = \pm 1)$. On the other hand, transitions with $\Delta J = 0$ and low values of J are most sensitive to changes in the dipole moment between the involved electronic states. The selection rules for M are $\Delta M = 0$ when the direction of the external field is parallel to the polarization of the laser pulses ($\vec{E}_{\mathrm{ext}} || \vec{E}_{h\nu}$, parallel case) and $\Delta M = \pm 1$ for them being oriented perpendicular to each other ($\vec{E}_{\mathrm{ext}} \perp \vec{E}_{h\nu}$, perpendicular case). The energy levels and intensities of the rotational transitions in a static electric field are calculated by describing the asymmetric rotor in the basis of symmetric rotor functions and including the Stark interaction terms.[29] A complete numerical implementation for near prolate asymmetric top molecules with the dipole moment directed along the *a*-axis of the molecule or cluster was presented recently by Moore et al.[30] and a more general solution with an arbitrary orientation of the dipole moment in the original and final states of the molecule by Kong and co-workers.[31]

IV. Experimental Results

A. $S_1 \leftarrow S_0$ Electronic Origin of BN. The S_1, $0^0 \leftarrow S_0$ transition of BN is of pure *b*-type[13] with $J' = J'' \pm 1$ and a missing Q branch. Considering the large value of the dipole moment in BN, a measurable Stark effect is expected for low J values even for moderate values of the external electric field within the resolution of our experiment. Figure 1a shows a detailed view of the central region of the BN S_1, $0^0 \leftarrow S_0$ UV spectrum from our previous work[13] for different values of an external electric field in the parallel case. Clearly an increased splitting of the rotational lines is observed with increasing field strength. Figure 1b shows the same spectral region for the perpendicular case. The transitions marked by (+,*) involve original and final states with $J = 1$ or 2 showing a splitting into two components in the parallel case (Figure 1a) and into three components in the perpendicular case (Figure 1b). The energy level diagram in Figure 2 visualizes the respective transitions in the parallel case. A noticeable increase of the dipole moment in the excited state would manifest itself as an increased lowering of the Stark levels in this electronic state. In consequence, all transitions from the ground to the S_1 state would be red-shifted compared to the field-free case. Since this is not found in the experiment (see case (+) in Figure 1a and

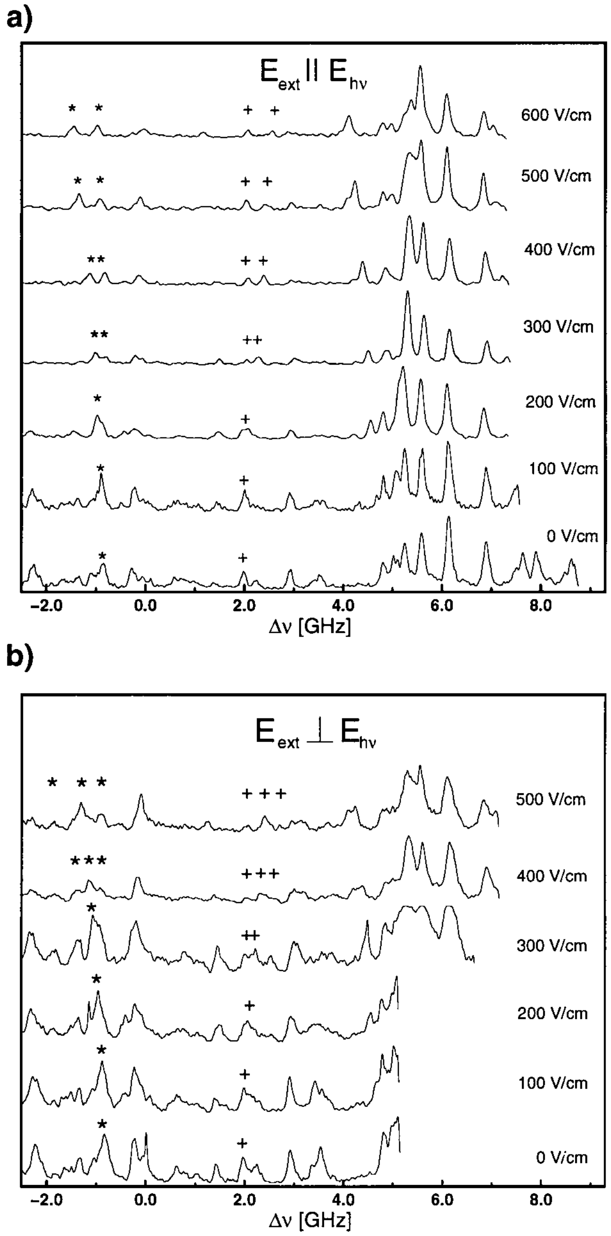


Figure 1. (a) Central part of the high-resolution REMPI spectrum of the $S_1 \leftarrow S_0$, 0_0^0 transition in BN measured for external electric fields 0 to 600 V/cm with the direction of the electric field parallel to laser polarization. (*) denotes the $|J'K_a'K_c'\rangle = |111\rangle \leftarrow |202\rangle$ transition with $\Delta J = -1$,(+) the complementary $|202\rangle \leftarrow |111\rangle$ transition with $\Delta J = +1$. (b) Same spectral region for the electric field perpendicular to the laser polarization. For an explanation, see text.

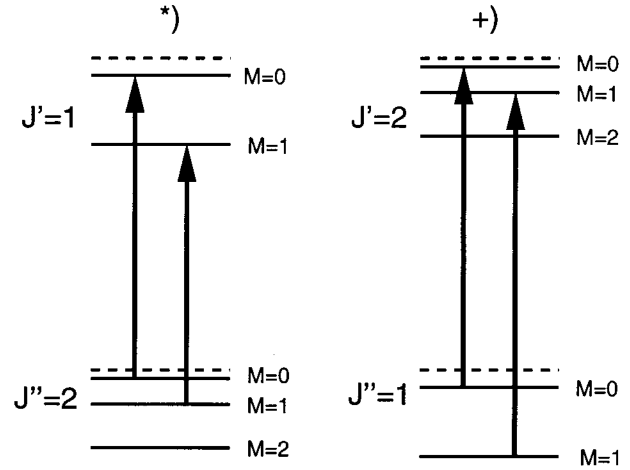


Figure 2. Scheme of the Stark levels involved in the complementary transitions of Figure 1 marked by * (left) and + (right). The dotted lines denote the zero field level of the rotational states, the arrows the allowed transitions when the electric field is parallel to the polarization of the excitation laser ($\Delta M = 0$). (*) $\Delta J = -1$: the shift to lower energies of the Stark levels in the given field is larger in the excited state leading to red-shifted transitions. (+) $\Delta J = +1$: the shift to lower energies of the Stark levels in the given field is smaller in the excited state leading to blue-shifted transitions.

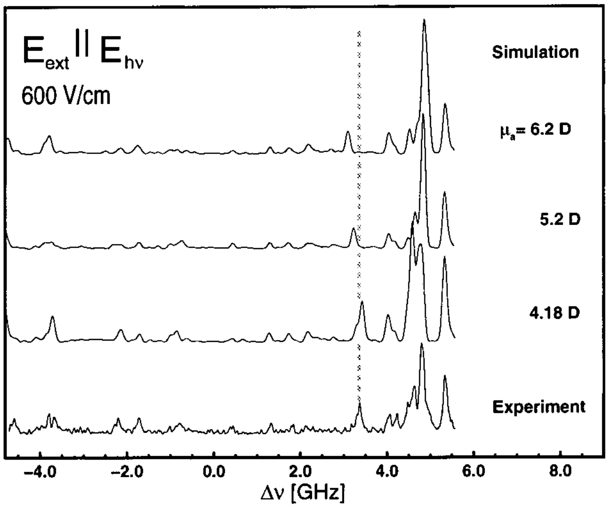
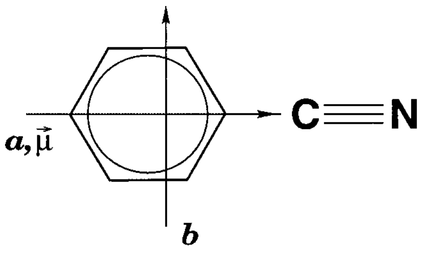


Figure 3. Bottom: Experimental spectrum of the center of the pure electronic band 0_0^0 of BN measured in an external field of 300 V/cm parallel to the laser polarization. Upper traces: Theoretical spectra for the rotational constants from Table 1 in the presence of the same electric field but different dipole moments in the S_1 state. The dotted line marks the $|110\rangle \leftarrow |101\rangle$, $M = 1$ transition most sensitive to a change of the dipole moment upon excitation. See text for discussion.

b), it is clear that the dipole moment of BN in the S_1 state does not increase strongly.

In a next step we simulated the Stark spectra using the program package of Moore et al.[30] with the known rotational constants for the S_0 ground[8] and the S_1 excited state.[13] The dipole moment $\vec{\mu}$ in the S_0 ground state is 4.18 D and directed along the a-axis of the molecule. The transition dipole moment in the observed b-type transition is directed perpendicular to the symmetry axis.



From the structure of BN in its S_1 state[13] one does not expect a change of the direction of the dipole moment in the excited state. Figure 3 shows theoretical spectra calculated for an increasing magnitude of the excited-state dipole moment in a constant electric field for the parallel case. The dotted line tags the experimental position of the $|110\rangle \leftarrow |101\rangle$ $(M'' = M' = 1)$ rotational line which is most sensitive to a change of the dipole moment upon excitation. The best fit to the measured spectrum is achieved for a value of 4.5(1) Debye for the excited-state dipole moment, in good agreement with the value of 4.45 D determined previously from a band contour analysis for the vibronic band at 513 cm^{-1} excess energy.[22] In the measured

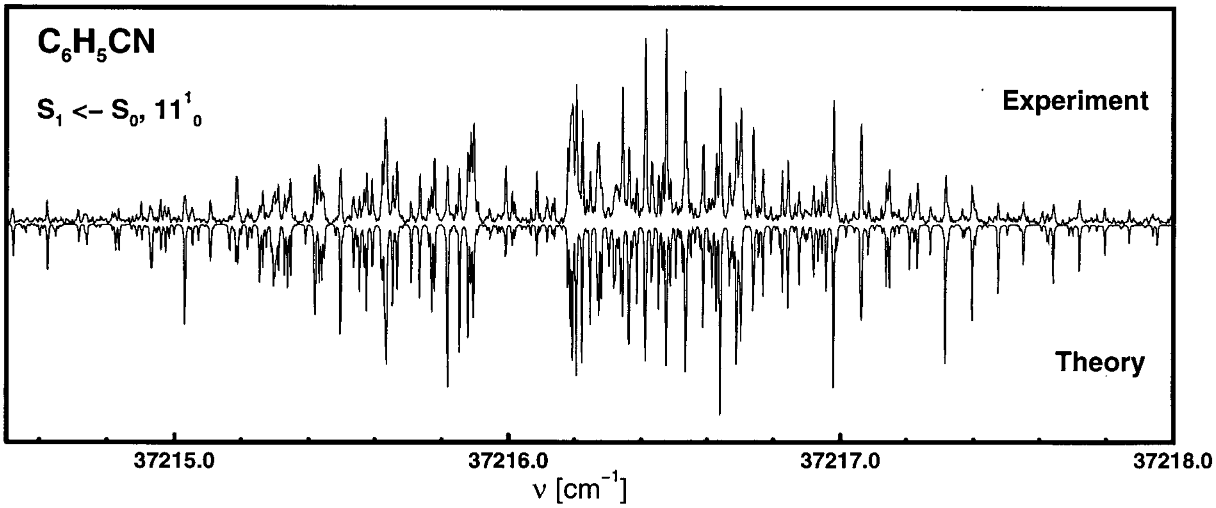


Figure 4. High-resolution REMPI spectrum of the BN $S_1 \leftarrow S_0$, 11^1_0 transition (upper trace) measured under field-free conditions (see text) and calculated spectrum (lower, inverted trace) using the fitted rotational constants.

TABLE 1: Experimental Rotational Constants *A*, *B*, *C*, Asymmetry Parameter τ, Band Origins (ν_0), and Dipole Moment μ_a of BN in the S_0 and S_1 States

	S_0[a]	S_1, 0^0 [b]	S_1, 11^1_0 [b]
A [$\mathrm{cm^{-1}}$]	0.188638(5)	0.18277(5)	0.18287(3)
B [$\mathrm{cm^{-1}}$]	0.05159814(5)	0.05042(3)	0.05034(2)
C [$\mathrm{cm^{-1}}$]	0.0405823(5)	0.03953(1)	0.03953(2)
τ	−0.851	−0.848	−0.849
ν_0 [$\mathrm{cm^{-1}}$]		36512.963(10)	37216.045(10)
μ_a [Debye]	4.18	4.5(1)	4.5(1)

[a] Ref 8. [b] This work.

energy range the spectra show no deviations from the simulation and hence no local perturbations were detected.

From Figure 1 it is clear that the electric fields present in the excitation region in a standard REMPI experiment (≈150 V/cm) lead to significant broadening and splitting of the rotational transitions of BN. Therefore we remeasured the S_1, $0^0 \leftarrow S_0$ spectrum under field-free conditions with a delayed pulsed extraction field. The resulting spectrum features a line width of less than 140 MHz for single rotational transitions which is close to our experimental resolution. A fit of the rotational constants reproduces well our recent experimental values.[13] The obtained rotational constants, the energy of the band origin, and the dipole moment in the ground and excited states are summarized in Table 1.

B. The 11^1_0 Band of the $S_1 \leftarrow S_0$ Transition of BN. To check whether there is a change of the dipole moment in vibrational states of BN at a higher excess energy in S_1, we measured the rotationally resolved REMPI spectrum of the 11^1_0 vibronic band at an excess energy of 703 $\mathrm{cm^{-1}}$ for different values of the external electric field. ν_{11} is a totally symmetric vibration and remarkable changes in the rotational constants of this band compared to the vibrational ground state are not expected. To ensure this, we first measured a high-resolution spectrum of the 11^1_0 vibrational band under field-free conditions which is shown in Figure 4 (upper trace) together with the theoretical spectrum using the fitted rotational constants (lower, inverted trace). The rotational constants (see Table 1) feature negligible changes compared to that of the vibrational origin band.

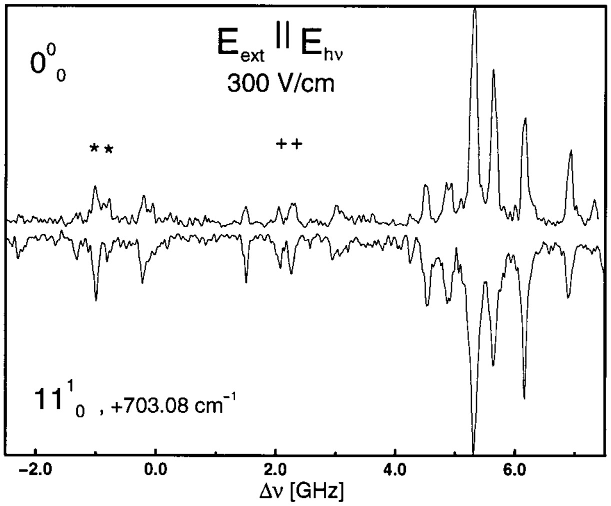


Figure 5. Comparison of the central part of the 0^0_0 (upper trace) and 11^1_0 (lower, inverted trace) bands at an excess energy of 703 $\mathrm{cm^{-1}}$ of BN measured in an electric field of 300 V/cm parallel to the laser polarization. The spectra are plotted on a common frequency scale relative to their origin. For discussion, see text.

Figure 5 shows a comparison of the central part of the vibronic origin band 0^0_0 (upper trace) and the 11^1_0 transition (lower inverted trace) in a static electric field of 300 V/cm. Except for the absolute shift of 703.08 $\mathrm{cm^{-1}}$ between the two vibronic bands, the spectra are identical. Thus the dipole moment is the same in both bands and there is no evidence of an increased coupling of the S_1, 11^1 state to a charge-transfer (RICT) state.

V. Summary and Conclusion

Benzonitrile (BN) constitutes a prototype system for charge-transfer processes after electronic excitation and has thus been investigated in a series of gas-phase experiments monitoring dispersed fluorescence. A significant change of the dipole moment in the excited state would be a direct indication of contributions from charge-transfer states. In this work we present for the first time high-resolution UV spectra of BN in a static electric field up to 700 V/cm displaying a Stark splitting of individual rotational lines. The analysis leads to an excited-state dipole moment of 4.5(1) Debye. Thus the dipole moment in the S_1 state is only slightly increased from the ground-state value of 4.18 D. In the measured spectra no local perturbations were detected. Stark splitting of the rotational transitions and thus the excited-state dipole moment is found to be identical in the electronic origin band 0_0^0 and the vibrationally excited 11_0^1 band at an excess energy of 703 cm^{-1}. From this we conclude that these low energy states are not coupled to a postulated RICT state. Future experiments will include the investigation of the dipole moments in other vibrational states at higher excess energies. Particularly bands including inducing modes for a RICT process, e.g., a bending motion of the cyano group, and the effects of polar solvents in their clusters with BN are promising candidates for a possible coupling. Here, the combination of theoretical methods to simulate the Stark spectra of asymmetric rotors[27,30,31] with the correlation automated rotational fitting technique (CARF)[13,32] is expected to be a powerful tool to analyze the Stark effect in the dense and congested UV spectra of these systems.

Furthermore, the results presented above demonstrate that it is necessary to achieve field-free excitation in high-resolution REMPI experiments of polar molecules in order to avoid broadening of the spectral features. In this work we have shown that even moderate electric fields of 100−200 V/cm which are present in state of the art REMPI experiments lead to a broadening and splitting of rovibronic transitions in molecules or clusters with a nonzero dipole moment.

Acknowledgment. The authors thank Davis T. Moore for providing his program for the simulation of asymmetric rotor spectra in electric fields. Financial support from the Sonderforschungsbereich 377 "*Photoionisation und Ladungstransfer in grossen Molekülen, Clustern und kondensierter Phase*" and the Fonds der Chemischen Industrie is gratefully acknowledged.

References and Notes

(1) Lippert, E.; Lüder, W.; Moll, F.; Nägele, W.; Boos, H.; Prigge, H.; Seibold-Blankenstein, I. *Angew. Chem.* **1961**, *73*, 695.
(2) Grabowski, Z. R.; Rotkiewicz, K.; Siemiarczuk, A.; Cowley, D. J.; Baumann, W. *N. J. Chim.* **1979**, *3*, 443.
(3) Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971.
(4) Zachariasse, K. A.; Grobys, M.; von der Haar, Th.; Hebecker, A.; Il'ichev, Yu. V.; Jiang, Y.-B.; Morawski, O.; Kühnle, W. *J. Photochem. Photobiol. A: Chem.* **1996**, *102*, 59.
(5) Sobolewski, A. L.; Domcke, W. *Chem. Phys. Lett.* **1996**, *250*, 428.
(6) Mordzinski, A.; Sobolewski, A. L.; Levy, D. H. *J. Phys. Chem. A* **1997**, *101*, 8221.
(7) Sakota, K.; Nishi, K.; Ohashi, K.; Sekiya, H. *Chem. Phys. Lett.* **2000**, *322*, 407.
(8) Casado, J.; Nygaard, L.; Sørensen, G. O. *J. Mol. Struct.* **1971**, *8*, 211.
(9) Dahmen, U.; Stahl, W.; Dreizler, H. *Ber. Bunsen-Ges. Phys. Chem.* **1994**, *98*, 970.
(10) Helm, R. M.; Vogel, H.-P.; Neusser, H. J.; Storm, V.; Consalvo, D.; Dreizler, H. *Z. Naturforsch.* **1997**, *52a*, 655.
(11) Melandri, S.; Consalvo, D.; Caminati, W.; Favero, P. G. *J. Chem. Phys.* **1999**, *111*, 3874.
(12) Storm, V.; Dreizler, H.; Consalvo, D. *Chem. Phys.* **1998**, *239*, 109.
(13) Helm, R. M.; Vogel, H.-P.; Neusser, H. J. *Chem. Phys. Lett.* **1997**, *270*, 285.
(14) Neusser, H. J.; Siglow, K. *Chem. Rev.* **2000**, *100*, 3921.
(15) Clara, M.; Siglow, K.; Neusser, H. J. *Z. Phys. Chem.* **2001**, *215*, 765.
(16) Förster, Th. *Z. Elektrochem.* **1939**, *45*, 548.
(17) Baumann, W.; Bischof, H.; Fröhling, J.-C.; Brittinger, C.; Rettig, W.; Rotkiewicz, K. *J. Photochem. Photobiol, A: Chem.* **1992**, *64*, 49.
(18) Baumann, W.; Nagy, *Z. Pure Appl. Chem.* **1993**, *65*, 1729.
(19) Mulliken, R. S. *J. Phys. Chem.* **1952**, *56*, 801.
(20) Nagakura, S. *J. Chem. Phys.* **1955**, *23*, 1441.
(21) Weast, R. C.; Astle, M. J. *Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1979.
(22) Muirhead, A. R.; Hartford, A.; Huang, K.-T.; Lombardi, J. R. *J. Chem. Phys.* **1972**, *56*, 4385.
(23) Huang, K.-T.; Lombardi, J. R. *J. Chem. Phys.* **1971**, *55*, 4072.
(24) Sussmann, R.; Neuhauser, R.; Neusser, H. J. *Can. J. Phys.* **1994**, *72*, 1179.
(25) Siglow, K.; Neusser, H. J. *J. Chem. Phys.* **2000**, *112*, 647.
(26) Okruss, M.; Müller, R.; Hese, A. *J. Chem. Phys.* **1999**, *110*, 10393.
(27) Korter, T. M.; Borst, D. R.; Butler, C. J.; Pratt, D. W. *J. Am. Chem. Soc.* **2001**, *123*, 96.
(28) Golden, S.; Wilson, E. B., Jr. *J. Chem. Phys.* **1948**, *16*, 669.
(29) Lombardi, J. R. *J. Chem. Phys.* **1968**, *48*, 348.
(30) Moore, D. T.; Oudejans, L.; Miller, R. E. *J. Chem. Phys.* **1999**, *110*, 197.
(31) Kong, W.; Bulthuis, J. *J. Phys. Chem. A* **2000**, *104*, 1055.
(32) Helm, R. M.; Neusser, H. J. *NATO ASI Series C* **1998**, *561*, 281.