J. Phys. Chem. 1987, 91, 4228-4231

Even though there is great practical benefit from evidence that ideal theories are reasonable approximations at small separations (10–30 Å) where these relations are expected to fail, we should not be lulled into complacency. Why do not we observe major deviations from ideality due to structure of the solvent, finite ion size, correlations, and fluctuations? What is the origin(s) of the short-range repulsion and its decay at large separations? Furthermore, does the exponential form for the close-range repulsion hold at very *close proximity*? The power-law attraction should overwhelm the repulsion to cause a precipitous collapse. Clearly, stiff-steric interactions must exist which are of ultimate importance in lamellar phase instability and bilayer coalescence at extreme dehydration.

Acknowledgment. This work was supported by the Medical Research Council of Canada through Grant MT 7477. E.A.E. is grateful to the Alexander von Humboldt Foundation, Federal Republic of Germany, for a Senior Scientist Award.

Registry No. CHOL, 57-88-5; SOPC, 14942-08-6; DOPE, 10015-88-0; DMPC, 13699-48-4; LysLeu$_{16}$Lys, 108260-43-1; LysLeu$_{24}$Lys, 108260-44-2.

ARTICLES

CH Overtones in Acetophenone and Benzaldehyde: Aryl and Methyl Local Modes

T. M. Abdul Rasheed, K. P. B. Moosad, V. P. N. Nampoori, and K. Sathianandan*

Laser Division, Department of Physics, Cochin University of Science & Technology, Cochin 682 022, India

(Received: October 16, 1986; In Final Form: March 17, 1987)

Vibrational overtone spectra of acetophenone and benzaldehyde in the visible and near-infrared regions are studied by the dual beam thermal lens and the conventional near-infrared absorption techniques. The observed increase in the mechanical frequency of the aryl CH bond from that of benzene is attributed to the decrease in the aryl CH bond length caused by the electron-withdrawing property of the substituents. Overtone spectra also demonstrate that acetophenone contains two types of methyl CH bonds arising from the anisotropic environments created by oxygen lone pair and carbonyl π electrons. The local-mode parameters of the two types of CH bonds are compared with those of acetone and acetaldehyde. The possible factors influencing the methyl CH bonds in acetophenone are discussed.

Introduction

Vibrational overtone spectroscopy of molecules containing X–H bonds (X = C, N, O) has been of renewed interest during the past few years.[1,2] The local-mode model is widely used for the description of overtone spectral features.[3-6] This model, introduced by Henry and Siebrand,[7] treats a molecule as a set of loosely coupled anharmonic oscillators localized on individual X–H bonds. Overtone spectra of X–H bonds have been reported for a wide variety of molecules like aromatics,[4] alkanes,[8] and haloalkanes.[9-12] These results have been successfully used for conformational analyses,[10,13] study of nonequivalent CH groups,[8] and substitution effects.[14-18] Such studies have also been extended to nonequivalent CH oscillators produced by anisotropic environments resulting from the lone pair electrons of oxygen and the π electrons of the carbonyl group.[19-23]

In the present paper, we report the overtone spectra of acetophenone and benzaldehyde in the visible and near-infrared regions obtained by dual beam thermal lens and conventional absorption techniques. The mechanical frequencies of the aryl CH bonds in both the molecules show higher values than the corresponding bond in benzene and is attributed to the electron-withdrawing effect of the two substituents. Acetophenone shows two methyl absorption bands arising from two types of CH bonds created by lone pair trans effects and π electrons of the carbonyl bond. The possible factors influencing the strengths of the two types of methyl CH bonds are discussed.

Experimental Section

High-purity acetophenone (99.9% Sisco Research Laboratories, India) and benzaldehyde (99.5% Glaxo BDH, India) are used for the present investigations. The fifth overtone spectra of aryl CH

---

(1) Henry, B. R. In *Vibrational Spectra and Structure*; Elsevier: New York, 1981; Vol. 10.

(2) Fang, H. L.; Swofford, R. L. In *Advances in Laser Spectroscopy*; Garetz, B. A., Lombardi, J. R., Eds.; Hayden: Philadelphia, PA, 1982.

(3) Henry, B. R. *Acc. Chem. Res.* **1977**, *10*, 207.

(4) (a) Swofford, R. L.; Long, M. E.; Albrecht, A. C.*J. Chem. Phys.* **1976**, *65*, 79. (b) Patel, C. K. N.; Tam, A. C.; Kerl, R. J. *J. Chem. Phys.* **1979**, *71*, 1470.

(5) Fang, H. L.; Swofford, R. L. *J. Chem. Phys.* **1980**, *72*, 6382.

(6) Fang, H. L.; Swofford, R. L. *J. Che. Phys.* **1980**, *73*, 2607.

(7) Henry, B. R.; Siebrand, W. *J. Chem. Phys.* **1968**, *49*, 4359.

(8) Wong, J. S.; Moore, C. B. *J. Chem. Phys.* **1982**, *77*, 603.

(9) Henry, B. R.; I-Fu-Hung. *Chem. Phys.* **1978**, *29*, 465.

(10) Henry, B. R.; Mohammadi, M. A. *Chem. Phys.* **1981**, *55*, 385.

(11) Mortensen, O. S.; Henry, B. R.; Mohammadi, M. A. *J. Chem. Phys.* **1981**, *75*, 4800.

(12) Rasheed, T. M. A.; Nampoori, V. P. N.; Sathianandan, K. *Chem. Phys.* **1986**, *108*, 349.

(13) Henry, B. R.; Thomson, J. A. *Chem. Phys. Lett.* **1980**, *69*, 275.

(14) Mizugai, Y.; Katayama, M. *J. Am. Chem. Soc.* **1980**, *102*, 6424.

(15) Mizugai, Y.; Katayama, M. *J. Am. Chem. Soc.* **1981**, *103*, 5061.

(16) Nakagaki, R.; Hanazaki, I. *Spectrochim. Acta* **1984**, *40A*, 57.

(17) Gough, K. M.; Henry, B. R. *J. Phys. Chem.* **1983**, *87*, 3804.

(18) Gough, K. M.; Henry, B. R. *J. Phys. Chem.* **1983**, *87*, 3433.

(19) Fang, H. L.; Swofford, R. L. *Appl. Opt.* **1982**, *21*, 55.

(20) Nakagaki, R.; Hanazaki, I. *J. Phys. Chem.* **1982**, *86*, 1501.

(21) Fang, H. L.; Meister, D. M.; Swofford, R. L. *J. Phys. Chem.* **1984**, *88*, 405.

(22) Fang, H. L.; Meister, D. M.; Swofford, R. L. *J. Phys. Chem.* **1984**, *88*, 410.

(23) Findsen, I. A.; Fang, H. L.; Swofford, R. L.; Birge, R. R. *J. Chem. Phys.* **1986**, *84*, 16.

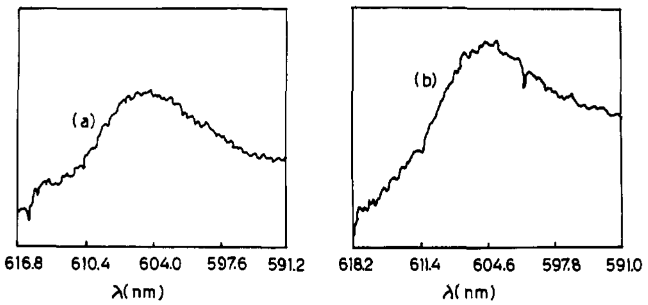

Figure 1. Overtone spectra of (a) acetophenone and (b) benzaldehyde in the $\Delta V = 6$ region recorded in pure liquid by dual beam thermal lens technique.

local modes of both the molecules are recorded with pure liquids by the dual beam CW thermal lens technique.[24] A Rhodamine 6G dye laser (Spectra Physics 380A) pumped by an argon ion laser (Spectra Physics 171-17) is used as the pump source. An output power of 50–100 mW is found suitable for the experiments. The pump beam chopped at 14 Hz is focused to a sample cell of path length 1 cm by a convex lens of focal length 15 cm. A 2-mW He–Ne laser beam passing through the sample probes the pulsating thermal lens formed in the sample. The modulated He–Ne beam then falls on a PMT (EMI 9684) placed at a distance of 130 cm from the sample cell. The PMT is fitted with a pinhole of 1 mm diameter and a He–Ne laser line filter. The output of the PMT is fed to a lock-in amplifier (EG&G PARC 124A) locked to the chopping frequency. The output of the lock-in amplifier and the relative power of the dye laser obtained from the wavelength corrected detector in the dye laser are fed to a ratiometer (EG&G PARC 193) for power normalization. The dye laser is scanned by using an inchworm translator (Burleigh) which turns the birefringent plate. Wavelength measurements are made with a wavemeter (Burleigh WA 20).

The overtone spectra for $\Delta V = 2$–4 are recorded in Hitachi 330 UV–vis–near-IR spectrophotometer. The $\Delta V = 3$ and 4 spectra are recorded in pure liquids with air as reference. For $\Delta V = 2$, the liquids are diluted by spectrograde carbon tetrachloride (99.9% Sisco Research Laboratories, India) to avoid saturation in the absorbance signals, and the spectra are recorded with carbon tetrachloride as the reference. The $\Delta V = 5$ spectra are not reported for both the compounds due to the poor signal to noise ratio of the spectrophotometer in that region.

Results and Discussion

One of the important observations reported here on the overtone spectra relates to the phenyl ring CH overtones. A local-mode analysis of the bands is carried out leading to a comparision of the mechanical frequencies with that of the benzene CH bond. In the case of acetophenone, two more progressions corresponding to two types of methyl CH bonds are identified. It was also possible to identify unambiguously the in-plane and out-of-plane modes leading to a comparison of their local-mode parameters with those of acetone and acetaldehyde. Possible factors influencing the strength of methyl CH bonds are also discussed. Aldehydic CH overtones of benzaldehyde are not studied in detail since such a study does not relate to the main objectives of the present investigation.

Aryl CH Bonds. The thermal lens spectra of the two compounds in the Rhodamine 6G region (Figure 1) are entirely due to the fifth overtone ($\Delta V = 6$) excitation of aryl CH bonds. The near-IR spectra (Figure 2–4) show absorption due to both aryl and methyl CH overtones in the $\Delta V = 2$,3, and 4 regions. The aryl CH overtones for $\Delta V = 2$, 3, 4, and 6 are represented by the Birge-Sponer equation

$$\Delta E_{v,0} = V(A + BV) \qquad (1)$$

A plot of $\Delta E/V$ vs. V gives the local-mode parameters, the mechanical frequency ($A - B$), and the anharmonicity B of the CH bonds. Table I shows the peak positions of the overtones and the local-mode parameters along with the least-squares correlation coefficients. It should be pointed out that, in spite of the fact that the number of data points for the Birge-Sponer plot is minimal, the good least-square fits obtained has fortunately helped in obtaining fairly accurate local-mode parameters for the aryl and the methyl CH bonds. The introduction of $-C(=O)CH_3$ and

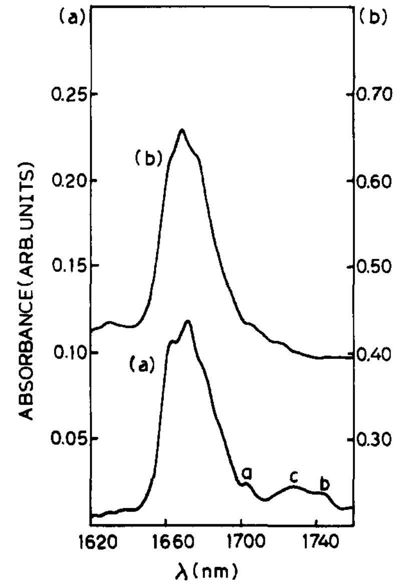

Figure 2. Overtone spectra of (a) acetophenone and (b) benzaldehyde in the $\Delta V = 2$ region. Samples were dissolved in carbon tetrachloride. Reference: carbon tetrachloride. C = combination (see text).

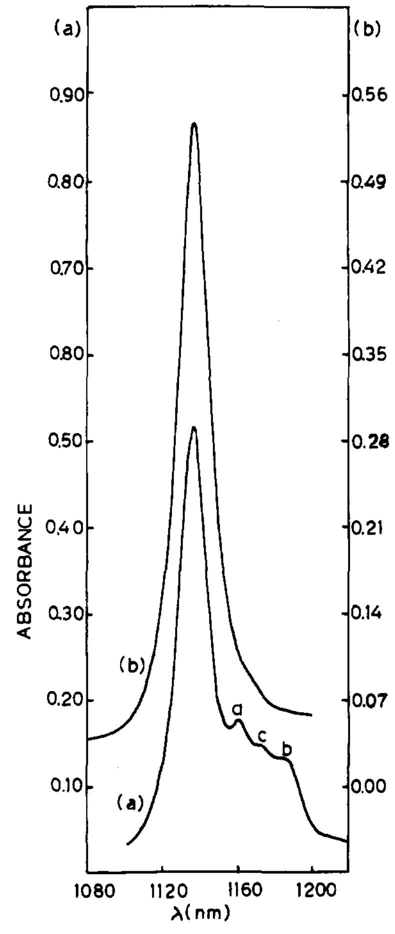

Figure 3. Overtone spectra of (a) acetophenone and (b) benzaldehyde in the $\Delta V = 3$ region. Pure samples. Reference: air. C = combination (see text).

---

(24) Fang, H. L.; Swofford, R. L. In *Ultrasensitive Laser Spectroscopy*; Kliger, D.S., Ed.; Academic: New York, 1983, and references therein.

TABLE I: Observed Overtone Energies (cm^{-1}), Mechanical Frequencies X_1 (cm^{-1}), Anharmonicities X_2 (cm^{-1}), Correlation Coefficients γ, and CH Bond Dissociation Energies ΔE_{max} (kcal/mol) for CH Overtone Spectra of Acetophenone and Benzaldehyde

	$\Delta V = 2$	$\Delta V = 3$	$\Delta V = 4$	$\Delta V = 5$	$\Delta V = 6$	X_1	X_2	γ	ΔE_{max}
benzene[a]	5983	8760	11442	14015	16467	3148.1	−57.6		118.55
acetophenone									
aryl CH	5981	8787	11468		16528	3165 ± 10	−59 ± 1.5	−0.99963	116.9
methyl CH$_a$	5869	8613	11211			3133 ± 8	−66 ± 1	−0.99978	102.1
methyl CH$_b$	5734	8432	11032			3027.5 ± 8	−54 ± 1.5	−0.99971	117.6
benzaldehyde									
aryl CH	5995	8799	11468		16541	3174 ± 12	−60 ± 2	−0.99922	115.5

[a] Data from ref 4b.

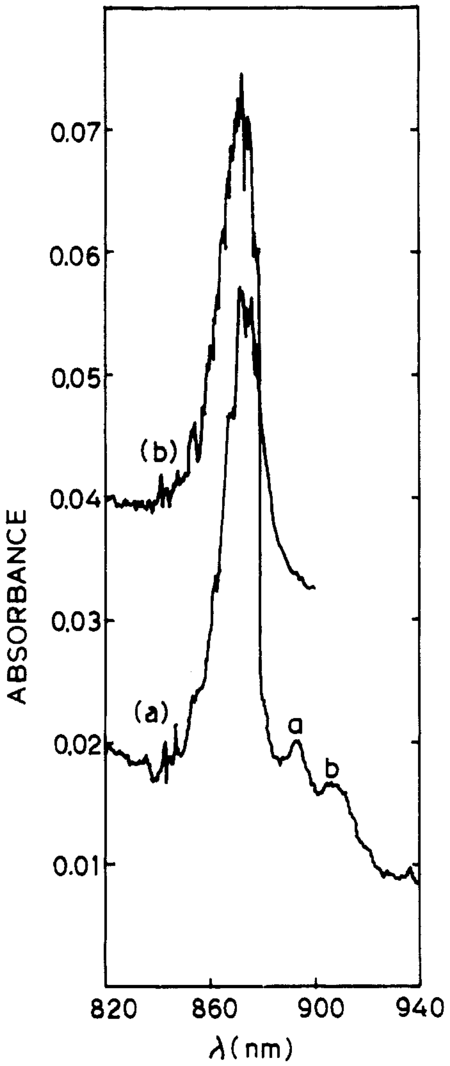

Figure 4. Overtone spectra of (a) acetophenone and (b) benzaldehyde in the $\Delta V = 4$ region. Pure sample. Reference: air.

TABLE II: Comparison of Methyl CH Local-Mode Parameters of Acetaldehyde, Acetone, and Acetophenone

molecule	X_1	X_2	ΔE_{max}
acetaldehyde[a]			
CH$_a$	3084 ± 13	−55 ± 2	119.2
CH$_b$	3083 ± 9	−63.3 ± 2	103.0
acetone[a]			
CH$_a$	3082 ± 9	−54 ± 1	121.3
CH$_b$	3047 ± 15	−58 ± 2	111.9
acetophenone			
CH$_a$	3133 ± 8	−66 ± 1	102.1
CH$_b$	3027.5 ± 8	−54 ± 1.5	117.6

[a] Data from ref 22.

–C(=O)H groups to the benzene ring shifts the aromatic CH overtone energies to higher values. It is also observed (Table I) that the anharmonicities of the aryl CH bonds in acetophenone and benzaldehyde are not very different from that of benzene CH local modes. But the mechanical frequencies are higher than that in benzene. Mizugai and Katayama[14] have studied the fifth aryl CH overtones of acetophenone and benzaldehyde by pulsed thermal lens technique and found that the aryl CH overtone energy is higher than that in benzene. They have correlated the shift of overtone energies with the inductive part of Hammet σ. But they have not attempted a detailed explanation on the increase of aryl CH force constant caused by the electron-withdrawing groups like –C(=O)CH$_3$ and –C(=O)H. Studies on other substituted benzenes[14,16,18] have also shown that electron-withdrawing groups cause an increase in the mechanical frequency (i.e., increase in the force constant) of the ring CH bonds while electron-donating groups cause a decrease in the mechanical frequency. An electron-withdrawing group reduces the electron density at the ring carbon atoms, and this in turn causes a greater attraction of the carbon atom for the valence electron cloud of the hydrogen atom. The net result is an increase in the CH force constant and hence the mechanical frequency. A reverse effect is expected for electron-donating substituents. Such effects were reported in the infrared studies[25] earlier.

The very small difference between the mechanical frequencies of aryl CH bonds in acetophenone and benzaldehyde shows that the major influence on the ring CH bonds originates from the carbonyl group. One would expect that the ortho, meta, and para CH bonds are likely to be affected differently by a substituent, the ortho being influenced most. A gas-phase study of selectively deuteriated samples would therefore be of interest to distinguish the different types of CH bonds present in the ring.

Methyl CH Bonds in Acetophenone. The bands indicated by a and b on the low-energy side of the aryl CH overtones individually fit into a Birge-Sponer plot with good correlation. The local-mode parameters along with the correlation coefficients are given in Table I. These two bands arise from the two different types of CH bonds present in the methyl group. A band appearing between the a and b bands in the $\Delta V = 2$ and 3 regions can only be assigned to a combination band involving the CH bending motion either from the ring or from the methyl group. In acetophenone, the phenyl ring, the C=O group, and one of the methyl CH bonds are in a plane. Also this methyl CH bond is cis to the C=O bond.[26] Thus the relative configuration of C=O and methyl group is the same as that in acetone and acetaldehyde.[22] We assign the high-energy component a of the methyl band to the in-plane CH bond and the low-energy component b to the two out-of-plane CH bonds. This assignment is in line with predictions of the "trans effect" theory and observations in compounds like acetone and acetaldehyde in the fundamental[27] and overtone[22,23] regions. As can be seen from Table II, in acetophenone the high-energy component has very large mechanical frequency and anharmonicity compared with acetone and acetaldehyde. Also, the mechanical frequency and anharmonicity of the low-energy component are slightly lowered with respect to acetone. It is known[22] that on going from acetaldehyde to acetone, the CH$_a$ peak is virtually unaffected while for the CH$_b$ oscillators, the mechanical frequency, and the anharmonicity are reduced. Fang et al.[22] have stated that this cannot be explained by the simple trans effect.

---

(25) Kaye, W. *Spectrochim. Acta* **1954**, *6*, 257.
(26) Potapov, V. M. *Sterochemistry*; MIR; Moscow, 1978; p 487.
(27) McKean, D. C. *Spectrochim. Acta, Part A* **1975**, *31A*, 861.

J. Phys. Chem. 1987, 91, 4231-4235

They have also pointed out that the smaller C=O bond length in acetaldehyde could result in an increased π electron interaction with the out-of-plane CH bonds. Considering the situation in acetophenone, it is known that C=O bond length in aryl alkyl ketones is larger than in dialkyl ketones.[28] This is clear from the decreased C=O group frequencies in aryl alkyl ketones. Thus our observation that the mechanical frequency and the anharmonicity of the out-of-plane CH_b bonds show decrease as we pass from acetone to acetophenone is in line with the arguments of Fang et al.; that is, in acetophenone the large C=O bond length results in a decreased interaction of π electrons with CH_b bonds. Another observation, as pointed out earlier, is that both the mechanical frequency and the anharmonicity of the in-plane CH_a bond in acetophenone are much larger than in acetone and acetaldehyde. It is known[28] that dipolar structures with decreased C=O bond order (increased C=O bond length) contribute much to aryl alkyl ketone structures. These structures are such that the carbonyl oxygen atom is very rich in electron density. The interaction of this electron cloud seems to be the main reason for the very large mechanical frequency and anharmonicity of the in-plane CH bond. The in-plane phenyl ring may also affect the strength of the CH_a bond. It can be seen from Table I that the dissociation energy of the CH_a bond is less than that of CH_b bonds. This is contrary to similar observations in other carbonyl compounds.[22] The CH_a potential curve in acetophenone is much shallower due to the large anharmonicity of this bond. As pointed out by Fang et al.,[22] the exact bond strengthening mechanism in carbonyl compounds needs further investigations.

Conclusions

Overtone spectroscopic studies of acetophenone and benzaldehyde by thermal lens spectroscopic and conventional methods are carried out. The aryl CH bonds of both the molecules show an increase of force constant over that in benzene. This is due to the electron-withdrawing property of the substituents. The methyl group of acetophenone shows two types CH bonds. Of the two, the in-plane C–H bond is assigned to the stronger force constant. The methyl CH bond parameters are compared to those of acetone and acetaldehyde. Possible factors influencing the mechanical frequency of CH bonds are discussed. A gas-phase study of selectively deuteriated compounds, though not studied here, will certainly yield more complete information on the overtone spectra of these compounds.

Acknowledgment. T.M.A.R. thanks the Department of Atomic Energy (India) for providing a Senior Research Fellowship and K.P.B.M. thanks CSIR (India) for providing a Senior Research Fellowship. The financial assistance from Department of Science and Technology is also gratefully acknowledged. We are grateful to Dr. Joseph Francis, Head of PS & RT Department, Cochin University, for permission to use the spectrophotometer and to Mr. T. Ravindran for help in recording the NIR spectra. We also thank Mr. Thomas Baby for experimental assistance and other research students of the laser division for their interest in the work.

---

[28] Margreta Avram; Mateescu, GH.D. *Infrared Spectroscopy—Applications in Organic Chemistry*; Wiley Interscience: New York, 1972; p 357.

High-Resolution Photoelectron Spectra of BrCN and ICN: Vibronic Mixing

Branka Kovač[†]

Rudjer Bošković Institute, Zagreb, Yugoslavia *(Received: December 18, 1986; In Final Form: April 10, 1987)*

High-resolution He I photoelectron (PE) spectra of BrCN and ICN have been measured and reexamined. Large spin-orbit splitting in the ground state of their molecular ions amounts to 1490 ± 40 and 4320 ± 40 cm^{-1}, respectively, in agreement with the previously obtained results. In the higher energy degenerate state ($\tilde{B}$), the splitting is reduced to 880 ± 40 and 1130 ± 40 cm^{-1}, respectively. Examination of the fine details observed in the three lowest systems reveals the activity of the $\nu_2(\pi)$ vibrational mode in addition to the totally symmetric ones, ν_1 and ν_3. Nonvanishing coupling between ($^2\Sigma^+$ and $^2\Pi_i$) and within ($^2\Pi_i$) electronic states takes place through the bending mode. Special attention is drawn to the complicated vibronic pattern in the overlapping region of $\tilde{A}/\tilde{B}$ systems in ICN.

Introduction

The electronic structure of cyanogen halide radical cations has received a great deal of attention,[1-9] but the effects accompanying the ionization process are still not understood. The four electronic systems appearing in the He I region correspond to two π and two σ ionizations, as expected on the basis of the molecular orbital (MO) configuration. The overall appearance of the photoelectron spectra (PE) of these 15 valence electron molecules is very similar, and the same types of vibrations are expected to be excited upon ionization. In spite of that, the $\tilde{B}$ systems in BrCN and ICN evaded explanation.[2,3] Complicated vibrational structure, in ICN in particular, was attributed to spin-orbit (SO) interaction, yet the fine details could not be analyzed due to insufficient resolution.[2,3] Recent results obtained from the emission spectra of supersonically cooled halocyanide cations[5] and their electronic absorption spectra in neon matrices[6] have shed more light on the spin–orbit mixing in the $\tilde{B}$ systems. Since the selection rules for emission/absorption spectra are different from those governing photoionization processes, the information available from the PE spectra is still valuable. For small molecules such as triatomics, high-resolution spectra may give an insight into geometry changes,[10] vibrational mixing,[11,12] and fine interactions which have been overlooked for many years until the observation of nontotally symmetric modes[13-16] had provoked a group of theoreticians[17] to

---

[†] No reprints available from the author.

[1] Heilbronner, E.; Hornung, V.; Muszkat, K. A. *Helv. Chim. Acta* **1970**, *53*, 347.

[2] Hollas, J. M.; Sutherley, T. A. *Mol. Phys.* **1971**, *22*, 213.

[3] Lake, R. F.; Thompson, H. *Proc. R. Soc. London, Ser. A* **1970**, *317*, 187.

[4] Allan, M.; Maier, J. P. *Chem. Phys. Lett.* **1976**, *41*, 231.

[5] Fulara, J.; Klapstein, D.; Kuhn, R.; Maier, J. P. *J. Phys. Chem.* **1985**, *89*, 4213.

[6] Leutwyler, S.; Maier, J. P.; Spittel, U. *J. Chem. Phys.* **1985**, *83*, 506.

[7] Bieri, G. *Chem. Phys. Lett.* **1977**, *46*, 107.

[8] Dibeler, V. H.; Liston, S. K. *J. Chem. Phys.* **1967**, *47*, 4548.

[9] Marthaler, O. Ph.D. Thesis, University of Basel, 1980.

[10] Cvitaš, T.; Klasinc, L. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1240.

[11] Cvitaš, T.; Güsten, H.; Klasinc, L. *J. Chem. Phys.* **1979**, *70*, 57.

[12] Cvitaš, T.; Klasinc, L.; McDiarmid, R. *Int. J. Quantum Chem. Symp.* **1984**, *18*, 537.