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Improved First Ionization Potential of the Dimethylsilaethylene Molecule Obtained with High-Temperature Photoelectron Spectroscopy

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The vacuum-ultraviolet photoelectron spectrum of the pyrolysis products of 1,1-dimethyl-1-silacyclobutane (DMSCB) has been recorded. The band associated with the first ionization potential of the 1,1-dimethyl-1-silaethylene (DMSE) molecule has been observed with vertical and adiabatic ionization potentials of 7.98 ± 0.01 eV and 7.71 ± 0.03 eV, respectively. Analysis of the observed vibrational structure in this band gave $\omega_e = 760 \pm 30$ cm^{-1} and this is assigned to excitation of the H_2C–Si< stretching mode in the ion. The experimental adiabatic ionization energy allows a lower limit for the heat of formation of $(Me_2Si{=}CH_2)^+$ to be derived as 745 ± 11 kJ mol^{-1}.

Introduction

The reluctance of silicon to form multiply bonded species has generated a great deal of interest both experimentally and theoretically in recent years. Since the classic experiments of Flowers and Gusel'nikov[1] which provided evidence for the formation of 1,1-dimethyl-1-silaethylene (DMSE) in the pyrolysis of 1,1-dimethyl-1-silacyclobutane (DMSCB), silaethylenes have been widely accepted as reaction intermediates.[2]

The first ionization potential (IP) of DMSE, produced by pyrolysis of DMSCB, has recently been measured by photoelectron spectroscopy.[3] A weak band showing no vibrational structure was observed associated with DMSE, and the vertical ionization potential (VIP) and the adiabatic ionization potential were measured as 8.30 ± 0.05 and 8.00 ± 0.05 eV, respectively. This latter value compares with estimates of the adiabatic first ionization potential of DMSE of 7.7 ± 0.4 and 7.5 ± 0.3 eV, respectively, obtained by electron impact mass spectrometry.[4,5] A higher-resolution PES study has also been performed on the silaethylene molecule.[6] The observed first vertical IP was in good agreement with a value predicted by a Δ(SCF) calculation corrected to allow for the electron correlation energy change on ionization. The resolved vibrational fine structure in the first PES band, showing double quanta excitation of the torsion vibration, was indicative of a twisted equilibrium structure in the ground state of the ion. Related studies have also been performed on silabenzene and silatoluene.[7,8]

A number of other spectroscopic studies have been performed. The gas-phase equilibrium geometry of DMSE has been determined by electron diffraction[9] although the structure obtained (particularly with regard to the Si=C distance) is not consistent with predicted geometries obtained for silaethylene and 1,1-dimethyl-1-silaethylene from ab initio molecular orbital calculations.[10-13] Also, the infrared spectrum of the pyrolysis products of DMSCB trapped in an inert gas matrix at low temperature has been recorded, and a number of bands have been assigned to vibrational modes of DMSE.[14-16]

In view of the rather low signal-to-noise ratio recorded for DMSE in the previous photoelectron investigation[3] and the rather poor agreement between values of the first adiabatic IP obtained from PES and mass spectrometry, it was decided to reinvestigate the photoelectron spectrum of DMSE in order to obtain an improved value for the first ionization potential.

Experimental Section

The DMSE molecule was produced within ≃2 cm of the photoionization region of the spectrometer by pyrolyzing DMSCB (Petrarch Systems Inc., 99.9% purity) heavily diluted in helium using an inductively heated, open-ended tantalum furnace. The temperature of the furnace when the highest yields of DMSE was observed was 1280 ± 10 K (estimated by focusing a calibrated optical pyrometer onto the hottest part of the furnace). Under these conditions, the temperature measured at ≃2 mm below the outlet of the furnace was 970 ± 10 K (measured with a chromel–alumel thermocouple).

The photoelectron spectrometer and the inductively heated furnace used in this study have both been described previously.[17,18] Spectral calibration was achieved by using

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(1) M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1968).

(2) (a) L. E. Gusel'nikov, *Acc. Chem. Res.* 8, 18 (1975); (b) M. Ishikawa, *Pure Appl. Chem.* 50, 11 (1978); (c) L. E. Gusel'nikov and N. S. Nametkin, *Chem. Rev.*, 79, 529 (1979).

(3) T. Koenig and W. McKenna *J. Am. Chem. Soc.*, 103, 1212 (1981).

(4) S. Basu, I. M. T. Davidson, R. Laupert, and P. Potzinger, *Ber. Bunsenges. Phys. Chem.*, 83, 1282 (1979).

(5) L. E. Gusel'nikov and N. S. Nametkin, *J. Organomet. Chem.*, 169, 155 (1979).

(6) P. Rosmus, H. Bock, B. Solouki, G. Maier, and G. Mihm, *Angew. Chem., Int. Ed. Engl.*, 20, 598 (1981).

(7) H. Bock, R. A. Bowling, B. Solouki, T. J. Barton, and G. T. Burns, *J. Am. Chem. Soc.*, 102, 429 (1980).

(8) B. Solouki, P. Rosmus, H. Bock, and G. Maier, *Angew. Chem., Int. Ed. Engl.*, 19, 51 (1980).

(9) P. G. Mahaffy, R. Gutowsky, and L. K. Montgomery, *J. Am. Chem. Soc.*, 102, 2854 (1980).

(10) Y. Yoshioka, J. D. Goddard, and H. F. Schaefer, *J. Am. Chem. Soc.*, 103, 2452 (1981).

(11) D. M. Hood and H. F. Schaefer, *J. Chem. Phys.*, 68, 2985 (1978).

(12) H. B. Schlegel, S. Wolfe, and K. Mislow, *J. Chem. Soc., Chem. Commun.*, 246 (1975).

(13) (a) R. Ahlrichs and R. Heinzmann, *J. Am. Chem. Soc.*, 99, 7452 (1977); (b) G. Trinquier and J. P. Malrieu, *ibid.*, 103, 6313 (1981).

(14) (a) A. M. Maltsev, V. N. Khabashesku, and O. M. Nefedov, *Dokl. Akad. Nauk SSSR*, 233, 421 (1977); (b) A. M. Maltsev, V. N. Khabashesku, and O. M. Nefedov, *Bull. Acad. Sci. USSR Chim.*, 5, 1165 (1976).

(15) V. G. Avakyan, L. E. Gusel'nikov, V. V. Volkova, and N. S. Nametkin, *Dokl. Akad. Nauk SSSR*, 254, 657 (1980).

(16) O. M. Nefedov, A. K. Maltsev, V. N. Khabashesku, and V. A. Korolev, *J. Organomet. Chem.*, 201, 123 (1980).

(17) D. Bulgin, J. M. Dyke, F. Goodfellow, N. Jonathan, E. Lee, and A. Morris, *J. Electron Spectrosc. Relat. Phenom.*, 12, 67 (1977).

(18) J. M. Dyke, N. Jonathan, and A. Morris, "Electron Spectroscopy: Theory, Techniques and Applications", Vol. 3, Academic Press, New York, 1979, p 189.

0022-3654/82/2086-2913$01.25/0

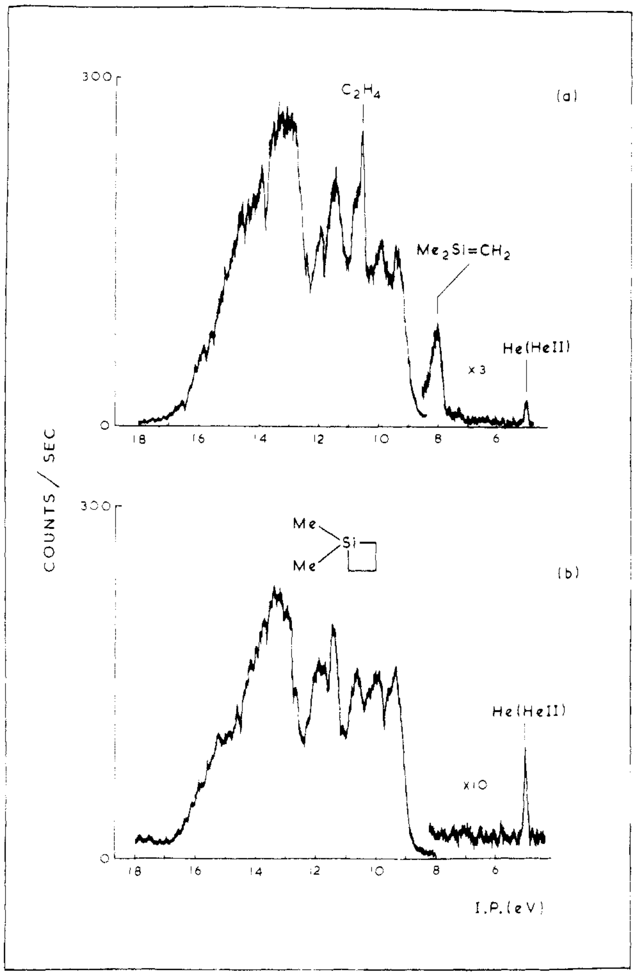

Figure 1. He I photoelectron spectrum of (a) pyrolyzed DMSCB at a furnace temperature of ≃1280 K and (b) DMSCB at room temperature. It should be noted that a higher partial pressure of DMSCB than that shown in b was used to obtain a. Ordinate: counts s^{-1}. Abscissa: ionization potential (eV).

the He Iα and He Iβ photoelectron spectra of methyl iodide and argon. Under the operating conditions of the experiment the usual resolution was 20–25 meV (fwhm) as measured for argon ionized with He Iα radiation.

Computational Details

In order to predict the first and higher ionization potentials of the DMSE molecule, restricted open-shell ab initio SCF calculations have been performed on DMSE and $(DMSE)^+$ using a double-ζ STO basis set.[19] Vertical ionization potentials for the first three ionic states produced by one-electron ionization from the neutral molecule have been predicted by using the Δ(SCF) method with the theoretically computed equilibrium geometry for the neutral molecule obtained via a series of ab initio calculations using a double-ζ plus polarization basis set.[10] This geometry was considered to be more reliable than the electron diffraction geometry[9] as the latter study gave a Si═C bond distance of 1.83 ± 0.04 Å (only 0.08 Å shorter than the Si—C single-bond distance in DMSE), whereas the theoretically predicted value is 1.692 Å.[10] Also, a recent single-crystal X-ray diffraction study on a silicon–carbon double-bonded species with bulky substituents attached to the silicon and carbon atoms gave a Si═C bond distance of 1.76 Å.[20] Because of steric interaction of the substituents, this value could be regarded as an *upper* limit for the Si═C bond distance in DMSE, consistent with a Si═C bond distance in DMSE in the range 1.69–1.71 Å.[10-12]

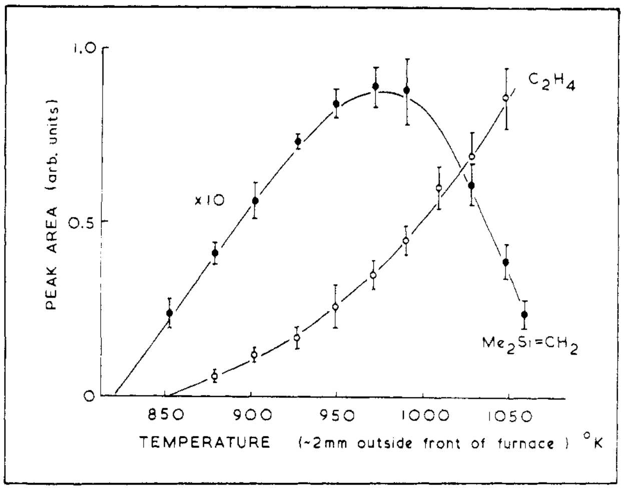

Figure 2. Variation of the intensities of the first bands of ethylene and DMSE as a function of temperature.

Results and Discussion

The He I photoelectron spectrum of DMSCB recorded in this investigation is shown in Figure 1b. It is in good agreement with that published previously.[21] Partial pyrolysis of DMSCB, heavily diluted in helium, at a furnace temperature of 1280 K yielded a spectrum of the type shown in Figure 1a. The most obvious additional features that appear on pyrolysis are a band at 10.51-eV ionization potential which can be assigned to ethylene and a band in the 7.0–9.0-eV IP region. This latter band was found to arise from ionization of a short-lived molecule as its intensity was very sensitive to the partial pressure of the inert carrier gas used. When no carrier gas was present, this band was observed only weakly whereas increasing the inert gas produced an initial intensity increase but further increase in carrier gas gave a decrease in intensity. On the basis of this evidence and because the main decomposition products of DMSCB are known to be DMSE and ethylene,[1] the band in the 7.0–9.0-eV IP region is assigned to ionization of the DMSE molecule.

It was estimated from the observed spectra that under optimum conditions for production of DMSE only about 20–30% of the parent molecule was pyrolyzed. Increasing the fraction of DMSCB pyrolyzed by using furnaces with a smaller exit hole (hence increasing the residence time in the furnace) gave rise to bands attributed to ethylene, acetylene, the methyl radical[22] as well as bands attributed to unpyrolyzed DMSCB. Under these conditions the band attributed to DMSE was not seen. Evidence for a small amount of 1,1,3,3-tetramethyl-1,3-disilacyclobutane was also found as the first band of this molecule occurs ≃0.7 eV lower than that of DMSCB.[21] However, because of the similarity of the photoelectron spectra of DMSCB and 1,1,3,3-tetramethyl-1,3-disilacyclobutane,[21] it was not possible to reliably estimate the relative partial pressures of these molecules at any given time.

Despite problems experienced with overlapping broad bands above 9.0-eV ionization energy, as the first bands of ethylene and DMSE are relatively sharp it was possible to measure their areas under conditions which gave the

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[19] C. Roetti and E. Clementi, *J. Am. Chem. Soc.*, **60**, 4725 (1974).

[20] (a) A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst, and R. K. Kallury, *J. Chem. Soc., Chem. Commun.*, 191 (1981); (b) A. G. Brook, private communication.

[21] C. S. Cundy, M. F. Lappert, J. B. Pedley, W. Schmidt, and B. T. Wilkins, *J. Organomet. Chem.*, **51**, 99 (1973).

[22] J. M. Dyke, N. Jonathan, E. P. F. Lee, and A. Morris, *J. Chem. Soc., Faraday Trans. 2*, **72**, 1385 (1976).

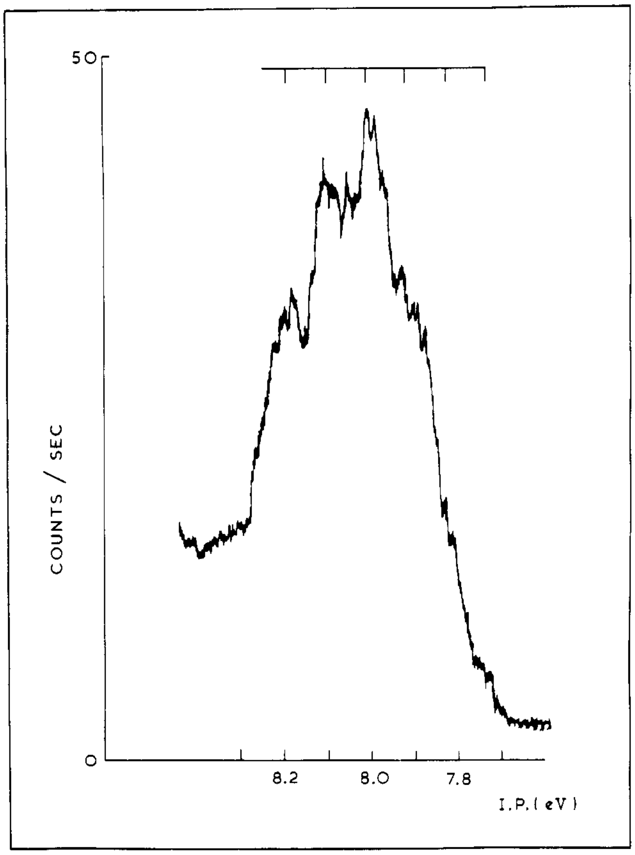

Figure 3. Expanded view of the band assigned to the first ionization potential of the DMSE molecule. Ordinate: counts s^{-1}. Abscissa: ionization potential (eV).

largest yield of DMSE. A plot of these areas as a function of the vapor temperature measured ≃2 mm away from the exit of the furnace is shown in Figure 2. This is very similar to a corresponding graph produced by a low-pressure pyrolysis study of DMSCB where the relative concentrations of the pyrolysis products were monitored by electron impact mass spectrometry.[4] This latter study showed that, because the signal detected in the mass spectrometer associated with the $(Me_2Si{=}CH_2)^+$ ion decreased to zero above 1000 K, removal of $Me_2Si{=}CH_2$ did not occur by reaction with ethylene or bimolecular recombination to give the disilacyclobutane under the low-pressure conditions of this experiment. As stated previously, because of overlapping band problems it was not possible to accurately monitor the relative concentrations of DMSCB and disilacyclobutane in the present PES study. However, under optimum conditions for production of DMSE no positive evidence for the formation of the disilacyclobutane was obtained. Hence, the temperature dependence shown in Figure 2 and its close correspondence with that given in ref 4 is taken as supporting evidence for the identification of the band shown in Figure 1a in the 7.0–9.0-eV region to DMSE.

An expanded spectrum of the first band of DMSE is shown in Figure 3. The vertical and adiabatic ionization potentials of the band have been measured as 7.98 ± 0.01 and 7.71 ± 0.03 eV, respectively. Six components of a vibrational series were also resolved in this band and analysis of this structure gave $\tilde{\omega}_e = 760 \pm 30$ cm^{-1} for the vibration excited in the ion. The ab initio calculations performed in this work show essentially that the first ionization potential of DMSE corresponds to removal of an electron from the carbon–silicon double bond. Hence, the $H_2O{-}Si$ equilibrium bond length will be greater in the ion than the neutral molecule, and it is expected that the $H_2C{-}Si$ stretching vibration will be excited in the ion on ionization. The infrared absorption spectrum of DMSE trapped at low temperature in an inert gas matrix shows an absorption at 1003.5 cm^{-1} which can be approximately described as a $H_2C{=}Si$ stretching mode.[14-16] Hence, reduction of this stretching frequency from 1003.5 cm^{-1} in the neutral molecule to 760 cm^{-1} in the ion is consistent with removal of an electron from the $H_2C{=}Si$ bond. Furthermore, it is known that silicon–carbon single-bond vibrational frequencies are typically in the region 640–780 cm^{-1} (ref 14–16 and 23) and the observed value in the first photoelectron band of DMSE is consistent with this.

TABLE I: Computed Vertical Ionization Potentials (eV) for 1,1-Dimethyl-1-silaethylene[a]

ionic state	Koopmans' theorem value from neutral molecule wave function	Δ(SCF)	exptl
$^2B_1$	8.10	6.77	7.98
$^2B_2$	12.15	11.08	
$^2A_1$	12.83	11.58	
$^2B_2$	14.72		

[a] The geometry used for these calculations is the minimum energy of ref 10.

The first band in the photoelectron spectrum of isobutene[24] is also very similar to the first band observed in the DMSE spectrum. A vibrational series is observed in the $C{-}CH_2$ stretching mode and this has been measured in this present study as 1320 ± 50 cm^{-1}. The corresponding value for the $C{=}CH_2$ stretching mode in the neutral molecule is 1661 cm^{-1} (ref 25), and the observed reduction in frequency on ionization is consistent with removal of an electron from the carbon–carbon double bond.[24] Comparison of the first vertical ionization potential of DMSE determined in this work (7.98 eV) with the corresponding values for ethylene (10.51 eV), silaethylene (8.97 eV),[6] and isobutene (9.42 eV) shows that on going from ethylene to isobutene the first VIP drops by 1.09 eV whereas on going from silaethylene to DMSE the first VIP drops by 0.99 eV. Similarly, comparing ethylene with silaethylene and isobutene with DMSE, reductions in the first vertical ionization potentials of 1.54 and 1.44 eV, respectively, are observed.

Further support for the assignment of the band in the 7.0–9.0-eV region to DMSE comes from the computed first vertical ionization potential (Table I). The computed Δ(SCF) value (6.77 eV) is, as expected, lower than the experimental value. However, allowance for correlation energy changes on ionization by an approximate method which relies on decomposition of a molecular wave function of an electronic state into its atomic components by a Mulliken population analysis[26] gives a corrected Δ(SCF) first vertical ionization potential of 8.14 eV, in good agreement with the experimental value of 7.98 eV. The corresponding corrected Δ(SCF) value using the electron diffraction geometry of ref 9 is 7.60 eV, showing a larger deviation from the experimental value. A number of higher ionization potentials of DMSE have been predicted (Table I) but these were not observed because of very

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(23) R. M. Irwin and J. Laane, *J. Phys. Chem.*, **82**, 2845 (1978).

(24) K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, "Handbook of He I PE Spectra of Fundamental Organic Molecules", Japan Scientific Societies Press, Tokyo, 1981.

(25) (a) C. M. Pathak and W. H. Fletcher, *J. Mol. Spectrosc.*, **31**, 32 (1969); (b) W. Lüttke and S. Braun, *Ber. Bunsenges. Phys. Chem.*, **71**, 34 (1967); (c) D. R. Smith, B. K. McKenna, and K. D. Möller, *J. Chem. Phys.*, **45**, 1904 (1966).

(26) (a) H. P. D. Liu and G. Verhaegen, *J. Chem. Phys.*, **53**, 735 (1970); (b) H. P. D. Liu and G. Verhaegen, *Int. J. Quantum Chem.*, **S5**, 103 (1971); (c) G. Verhaegen and C. M. Moser, *J. Phys. B*, **3**, 478 (1970).

intense broad bands above 9.0 eV ionization energy mainly arising from unpyrolyzed DMSCB (Figure 1a).

The adiabatic first ionization potential of DMSE determined in this work, 7.71 ± 0.03 eV, should allow a determination of the heat of formation of $(Me_2Si{=}CH_2)^+$ from the known heat of formation of the neutral molecule. However, although the vibrational structure in Figure 3 was regularly spaced and could be assigned to vibrational excitation of the ion, contributions from ionization of a vibrationally excited neutral molecule to Figure 3 cannot be ruled out. Hence the measured adiabatic IP is regarded as a lower limit for the true adiabatic IP. The heat of formation of neutral DMSE has recently been determined from the proton affinity of $Me_2Si{=}CH_2$ measured by ion cyclotron resonance spectroscopy.[27] However, the value derived from this work depends on the heat of formation of the trimethylsilyl ion. A more precise value for this quantity than that used in the original work (ref 27) is, however, available which lowers the heat of formation of $Me_2Si{=}CH_2$, $\Delta H_f{}^\circ{}_{298}$, to 2 ± 9 kJ mol^{-1}.[28,29] This latter value combined with the lower limit for the adiabatic IP determined in this work yields a lower limit for the heat of formation of $(Me_2Si{=}CH_2)^+$ of 745 ± 11 kJ mol^{-1}.

In conclusion, the main piece of information to be derived from this investigation is an improved value for the first ionization potential of the DMSE molecule. The figure obtained is significantly lower than that measured in a previous PES investigation[3] but is in reasonable agreement with estimates obtained by electron impact mass spectrometry.[4,5]

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(27) W. J. Pietro, S. K. Pollack, and W. J. Hehre, *J. Am. Chem. Soc.*, **101**, 7126 (1979).

(28) P. Potzinger, B. Reimann, and R. S. Roy, *Ber. Bunsenges. Phys. Chem.*, **85**, 1119 (1981).

(29) G. Distefano, *Inorg. Chem.*, **9**, 1919 (1970).

Vibronic Absorption Spectra of Naphthalene and Substituted Naphthalene Cations in Solid Argon

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Naphthalene and methyl- and halonaphthalene cations have been produced by one- and two-photon matrix photoionization techniques and trapped in solid argon for absorption spectroscopic study. Five transitions in the visible and ultraviolet regions have been assigned to the radical cations. The argon matrix absorption spectra are in agreement with photoelectron and photodissociation spectra, absorption spectra of the ions in Freon glasses, and simple HMO calculations. Substituent effects were observed for the origins of the five transitions. The repeating vibronic intervals in the red N^+ transitions due to the C(9)–C(10) stretching fundamentals for this group of substituted naphthalene cations are 40–50 cm^{-1} *above* the Raman fundamentals for the molecules whereas the vibronic intervals due to ring deformation modes are up to 30 cm^{-1} *below* the appropriate Raman fundamentals, and vibronic intervals in the sharp UV band are 30–45 cm^{-1} *below* Raman fundamentals, which correlate with HMO π bond orders.

Introduction

A substantial amount of research has been done recently on the optical spectroscopy of molecular cations in noble gas matrices. These studies have included a variety of cations such as hexafluorobenzene,[1] fluorine-substituted benzene,[2] diacetylene,[3] methylene chloride,[4] carbon tetrachloride,[5] cycloheptatriene,[6] and styrene cations.[7] The former studies of more stable cations have relied heavily on gas-phase emission and photoelectron spectra for identification of the cation carrier whereas the latter studies of photosensitive cations have involved photochemistry and employed gas-phase photodissociation and photoelectron spectra for identification of the cation spectrum.

Naphthalene has been studied extensively by photoelectron spectroscopy.[8-11] Absorption spectra of the naphthalene cation (hereafter N^+) and methyl-substituted naphthalene cations have been observed in a variety of glassy matrices,[12-14] and a preliminary argon matrix absorption spectrum has been communicated.[15] Owing to the high endothermicity of N^+ photodissociation,[16] N^+ has

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(1) Bondybey, V. E.; English, J. H.; Miller, T. E. *J. Am. Chem. Soc.* **1978**, *100*, 5252; *J. Chem. Phys.* **1980**, *73*, 3053.

(2) Bondybey, V. E.; Miller, T. E.; English, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 1248.

(3) Bondybey, V. E.; English, J. H. *J. Chem. Phys.* **1979**, *71*, 777.

(4) Andrews, L.; Prochaska, F. T.; Ault, B. S. *J. Am. Chem. Soc.* **1979**, *101*, 9.

(5) Andrews, L.; Prochaska, F. T. *J. Phys. Chem.* **1979**, *83*, 368, and new data to be published.

(6) Andrews, L.; Keelan, B. W. *J. Am. Chem. Soc.* **1980**, *102*, 5732.

(7) Andrews, L.; Harvey, J. A.; Kelsall, B. J.; Duffey, D. C. *J. Am. Chem. Soc.* **1981**, *103*, 6415.

(8) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. "Molecular Photoelectron Spectroscopy"; Wiley-Interscience: New York, 1970.

(9) Eland, J. H. D.; Danby, C. J. *Z. Naturforsch. A* **1968**, *23*, 355.

(10) Clark, P. A.; Brogli, F.; Heilbronner, E. *Helv. Chem. Acta* **1972**, *55*, 1415.

(11) Maier, J. P.; Haselbach, E., personal communication.

(12) Badger, B.; Brocklehurst, B. *Trans. Faraday Soc.* **1969**, *65*, 2588.

(13) Shida, T.; Iwata, S. *J. Am. Chem. Soc.* **1973**, *95*, 3473.

(14) Haselbach, E.; Bally, T.; Gschwind, R.; Klemm, U.; Lanyiova, Z. *Chimica* **1979**, *33*, 405.

(15) Andrews, L.; Blankenship, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 5977.

0022-3654/82/2086-2916$01.25/0