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He(I) Photoelectron Spectroscopy and Electronic Structure of Alkyllithium Clusters

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The electronic structure of some alkyllithium clusters has been investigated by He(I) photoelectron spectroscopy. Two distinct types of spectra have been observed. This is explained by the different degree of association of the compounds in the gas phase, as determined by the steric demand of the alkyl substituent. From the analysis of the spectra it can be concluded that isopropyl- (*i*-PrLi), *sec*-butyl- (*s*-BuLi), and *tert*-butyllithium (*t*-BuLi) form only tetramers, while ethyl- (EtLi), *n*-propyl- (*n*-PrLi), *n*-butyl- (*n*-BuLi), and isobutyllithium (*i*-BuLi) are mixtures of tetrameric and hexameric clusters in the gas phase. This observation is in accord with former mass spectrometric investigations [Plavšić, D.; Srzić, D.; Klasinc, L. *J. Phys. Chem.* **1986**, *90*, 2075; Berkowitz, J.; Bafus, D. A.; Brown, T. L. *J. Phys. Chem.* **1961**, *65*, 1380]. The band shapes and intensities are interpreted by large geometry changes taking place during the ionization as a consequence of Jahn−Teller distortion of the ionic clusters and the change of electrostatic interactions. The nature and extent of the distortion is examined by ab initio quantum chemical calculations. The effect of the substituents and the degree of association on the electronic structure is also clarified.

1. Introduction

The geometry and electronic structure of alkyllithium compounds have been extensively studied due to their importance in organic and organometallic synthesis as well as in catalysis. It is well known that they form clusters containing multicentered bonds not only in the solid state and in solution but also in the gas phase because of their electron-deficient nature. The usual number of alkyllithium (LiR) units forming the clusters is 2, 4, or 6; however in certain cases larger or odd-membered aggregates have also been observed.[1−3]

Weiss et al. have investigated the structure of solid methyllithium (MeLi) by X-ray[4,5] and neutron diffraction.[6] These studies confirm tetrahedral lithium cores with pyramidal methyl groups placed on each face in staggered orientation relative to the lithium atoms. EtLi[7,8] and *t*-BuLi[9] have also been observed as tetramers, while *i*-PrLi,[10] *n*-BuLi,[9] cyclohexyllithium,[11] and 2,2,3,3-tetramethylcyclopropyllithium[12] have been found to be hexamers in the crystalline state.

According to freezing point depression measurements,[13−18] ^{1}H, ^{6}Li, ^{7}Li, and ^{13}C NMR,[19−29] and IR[15,25,30−34] spectrometric investigations, the degree of association in solution depends not only on the steric bulk of the substituent but also on the solvent, the temperature, and the concentration. As an example,

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EtLi and *n*-BuLi form hexameric clusters, and *t*-BuLi form tetrameric clusters in hexane and benzene, while both *n*-BuLi and *t*-BuLi are a mixture of tetramers and hexamers in Nujol, as found by fast atom bombardment mass spectrometric investigations.[35] Some further examples have recently been reviewed by Lukehart in ref 1.

The abundance of each type of cluster in the gas phase is determined mainly by their thermodynamic stability, the pressure, and temperature. Nevertheless, the abundance may also be affected by the structure of the crystal the sample is evaporated from and the gas-phase reaction rates between these clusters. One of the first gas-phase experiments on an alkyllithium compound was performed by Berkowitz et al.[36] in 1961. They have investigated the vapor of EtLi using electron impact mass spectrometry. With the aid of a double-chambered, separately heated Knudsen cell, roughly equal hexamer and tetramer concentrations were observed at 80−95 °C. This result was confirmed later by Brown et al.[37] The gas-phase structure of *t*-BuLi has been probed by photoionization mass spectrometry by McLean et al.,[38] who detected only tetramers at room temperature. Analyzing the photoionization efficiency curve, they have additionally determined the ionization potential of $(t\text{-BuLi})_4$, which is 6.2 eV. Using flash vaporization mass spectrometry, Chinn and Lagow[39] characterized the MeLi vapor as consisting of tetramers only. In 1986, Plavšić, Srzić, and Klasinc[40] performed a detailed electron impact and photoionization mass spectrometric investigation of alkyllithium compounds. In agreement with the previous results, they have concluded that MeLi, *i*-PrLi, *s*-BuLi, and *t*-BuLi consist of tetrameric clusters only, while *n*-PrLi, *n*-BuLi, and *i*-BuLi form mixtures of tetramers and hexamers in the gas phase. The same group also presented the photoelectron spectra of *s*-BuLi and *i*-PrLi;[41] however, they have not investigated compounds with other substituents that may form hexamers in the gas phase.

As an extension of the above-mentioned photoelectron spectroscopic investigations, the influence of cluster size and the inductive effect of the substituent on the ionization energies are examined in this paper. The low-energy region of the photoelectron spectra is analyzed in more detail.

2. Experimental Section

A. Sample Preparation. EtLi, *n*-PrLi, *i*-PrLi, and *i*-BuLi were prepared by standard procedures, i.e., by the reaction of the corresponding alkyl bromide (or alkyl chloride) with lithium in hexane at 0 °C. Hexane was removed in vacuo at 20−100 °C. All operations, including introduction of the sample to the spectrometer, have been carried out in an inert atmosphere. The solutions of *n*-BuLi, *s*-BuLi, and *t*-BuLi in hexane or in pentane were obtained from Aldrich Company and were worked up and handled similarly.

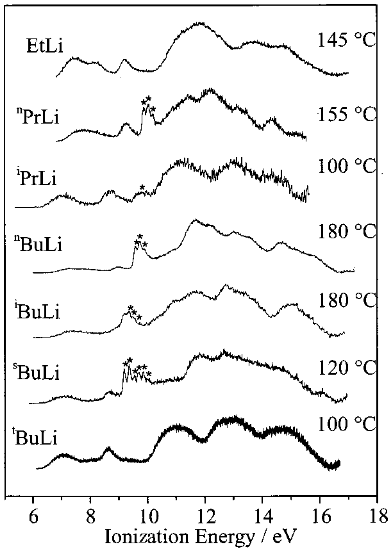

Figure 1. He(I) photoelectron spectra of alkyllithium compounds. (Bands due to decomposition products are marked by asterisks.)

B. He I Photoelectron Spectroscopic Measurements. He I photoelectron (PE) spectra were recorded on an ATOMKI ESA-32 spectrometer[42] at 100−180 °C using a heated direct inlet probe. The sample pressure in the ionization chamber was estimated to be $(1-2) \times 10^{-5}$ mbar. All spectra were calibrated against argon or the alkene decomposition products of the investigated compounds as internal standards; the background was corrected by a Shirley-type function. Resolution at the $^2P_{3/2}$ peak of argon was 25−100 meV. The maximum error in ionization energies is estimated to be less than 0.05−0.1 eV.

C. Ab Initio Calculations. Ab initio quantum chemical calculations have been performed for the neutral $(\text{MeLi})_n$ ($n = 4, 6$) clusters at the RHF/6-31G** and RB3LYP/6-31G** as well as for the ionic $(\text{MeLi})_n^+$ clusters at the UHF/6-31G** and UB3LYP/6-31** levels of theory. Geometry optimizations and vibrational frequency calculations have been carried out by the PQS 2.1 program system[43] of Pulay and co-workers, while the outer-valence Green's function (OVGF) ionization energies were obtained by Gaussian94.[44]

3. Results

The He(I) PE spectra are shown in Figure 1. The 6−10 eV region of the spectra—with smaller energy steps and longer data acquisition time—is presented in Figure 2. Ionization energies are listed in Table 1.

4. Discussion

A. Geometry of the Neutral Clusters. Calculated geometry parameters of the neutral tetrameric and hexameric MeLi clusters, results of previous ab initio

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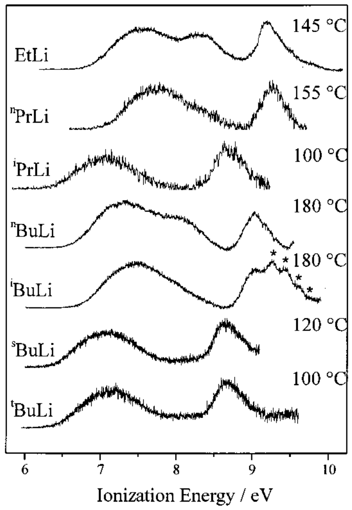

Figure 2. Low-energy region of He(I) photoelectron spectra of alkyllithium compounds. (Bands due to decomposition products are marked by asterisks. See text for assignments.)

Table 1. Experimental Ionization Energies (in eV) of Alkyllithium Compounds

compound	1st adiabatic	1st vertical	2nd vertical	3rd vertical
EtLi	6.75	7.60	8.40	9.20[b]
n-PrLi	6.80	7.60	8.20[a]	9.30[b]
i-PrLi	6.35	7.15	8.70[b]	
n-BuLi	6.60	7.35	8.10	9.00[b]
i-BuLi	6.55	7.40	8.00[a]	9.00[b]
s-BuLi	6.30	7.15	8.70[b]	
t-BuLi	6.25	7.15	8.70[b]	

[a] Shoulder. [b] Ionization from same type (a_{1g}) of orbitals. See text for details.

calculations,[29,45–56] and related experimental results are presented in Tables 2 and 3. According to earlier conclusions of Schleyer et al.,[52] the hydrogen atoms in the tetrahedral (T_d) tetrameric cluster (Figure 3a) were constrained to be in an eclipsed conformation, while in the case of the hexameric cluster only the most stable isomer having D_{3d} symmetry (Figure 3b) was considered, which is the only isomer observed experimentally.[9–12,54]

The geometric parameters of the tetrameric and hexameric clusters reveal that the lithium–carbon and lithium–lithium bond distances are rather similar, while the carbon–carbon distance in the hexamer is significantly shorter than that in the tetramer. As it has been suggested earlier,[25] this tighter packing of carbon atoms could prevent the formation of hexamers with bulky substituents.

Table 2. Interatomic Distances (in Å) for Tetrameric (T_d) Methyllithium

method	r_{C-C}	r_{C-Li}	r_{Li-Li}	reference
PRDDO	3.46	2.09	2.18	49
MNDO		2.197		29
HF/STO-3G		2.250	2.369	29, 46, 47, 48
HF/3-21G		2.236	2.420	52
HF/6-31G**	3.637	2.229	2.433	this work
HF/6-31+G*		2.228	2.430	55
B3LYP/6-31G**	3.579	2.196	2.404	this work
MP2/6-31+G*	3.582	2.188	2.363	55
X-ray diffraction[a,b]		2.31	2.68	4,5
neutron diffraction[a,b]	3.511	2.209	2.605	6
neutron diffraction[a,c]	3.621	2.256	2.591	6

[a] In contrast to the “gas-phase” ab initio calculations, the crystal-phase diffraction experiments established the staggered conformation. For details see ref 55. [b] Determined at 290 K. [c] Determined at 0 K.

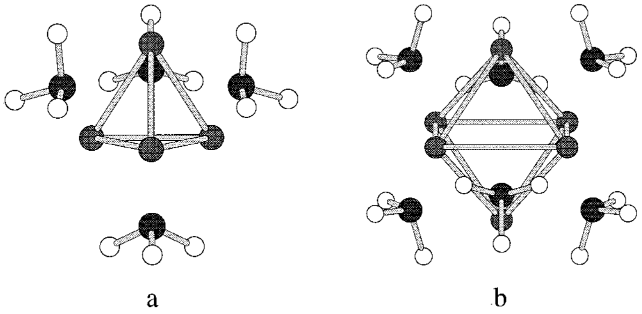

Figure 3. Structure of (a) tetrameric (T_d) and (b) hexameric (D_{3d}) methyllithium clusters.

B. Electronic Structure and Photoelectron Spectra. The valence-shell energy-level diagram together with the Hartree–Fock orbital energies of tetrameric (T_d) and hexameric (D_{3d}) MeLi clusters are presented in Figure 4. In the case of the tetrahedral cluster, the highest occupied molecular orbital (HOMO) is a triply degenerate orbital (t_{2g}), which is separated by about 2 eV from the nondegenerate, penultimate a_{1g} orbital (HOMO-1). Since the lithium core of the hexamers is a slightly distorted octahedron, the energies of the HOMO (b_g) and HOMO-1 (e_g) are almost identical. These orbitals are well separated from a doubly degenerate (e_g) and a nondegenerate (a_{1g}) orbital by about 1 and 2 eV, respectively.

Assuming that this qualitative MO scheme holds generally for alkyllithium compounds, the following bands are expected in the low-energy region of the PE spectrum: two bands (${t_{2g}}^{6-1}$ and ${a_{1g}}^{2-1}$) for tetrahedral clusters and three bands (${b_g}^{2-1}$+${e_g}^{4-1}$, ${e_g}^{4-1}$, and ${a_{1g}}^{2-1}$) in the case of hexameric (D_{3d}) clusters. If interpretation of the PE spectra is based on this MO scheme, it can be concluded that *i*-PrLi, *s*-BuLi, and *t*-BuLi form tetramers (here after referred to as class A compounds), while EtLi, *n*-PrLi, *n*-BuLi, and *i*-BuLi consist of hexamers (here after referred to as class B compounds). In the latter case it is also possible that a mixture of tetramers and hexamers is present in the gas phase, because according to Koopmans’ theorem, the first and the second ionization energies of the tetramers are much the same as the first (i.e., ${b_g}^{2-1}$+${e_g}^{4-1}$) and the third

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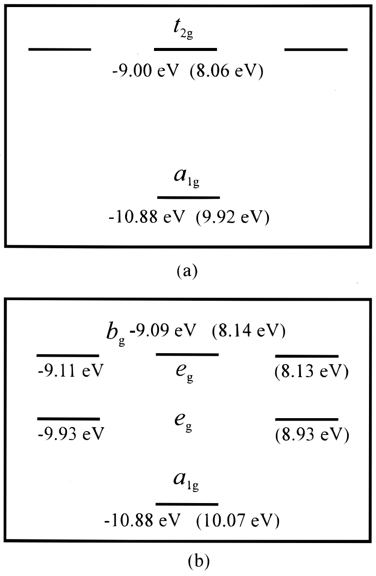
Table 3. Interatomic Distances (in Å) for Hexameric (D_{3d}) Methyllithium[a]

method	r_{C-C} (r'_{C-C})	r_{C-Li} (r'_{C-Li})	r_{Li-Li} (r'_{Li-Li})	reference
PRDDO	3.79	2.09	2.20	49
HF/3-21G		2.19 (2.29)	2.44 (2.96)	56
HF/4-31G		2.180 (2.284)	2.433 (2.953)	54
HF/6-31G**	3.543 (4.146)	2.182 (2.281)	2.456 (2.987)	54, this work
B3LYP/6-31G**	3.486 (4.098)	2.151 (2.250)	2.423 (2.932)	this work

[a] *r*, shortest values; *r′*, second shortest values.



(a)

(b)

Figure 4. Valence-shell energy-level diagram and RHF/6-31G** orbital energies of (a) tetrameric (T_d) and (b) hexameric (D_{3d}) methyllithium clusters. (OVGF/6-31G**//RHF/6-31G** ionization energies are given in parentheses.)

ionization energies of the hexamers. This possibility is also indicated by the fact that intensity ratios in these spectra vary slightly on temperature change. (As our instrument is not supplied by a separately heated inlet probe and ionization chamber, we were not able to investigate the temperature dependence of spectra in a range wider than 10–15 °C.) This classification of the investigated compounds, as well as the mixture-like nature of the class B compounds, is consistent with former mass spectrometric investigations.

The calculated OVGF/6-31G** ionization energies are also presented, in parentheses, in Figure 4. These values are closer to the experimental ones by about 1 eV, while the ordering and the energy difference between the different states—supporting the above assignments—is much the same as it has been obtained by Koopmans' theorem. Most of the remaining differences between the calculated and the experimental vertical ionization energies are thought to be caused by the different inductive effects of the methyl substituent and the alkyl groups of the experimentally studied compounds.

C. Effect of Cluster Size and Alkyl Substituents on the Ionization Energies. Both Berkowitz et al.[36] and Klasinc et al.[40] have reported similar abundances for the tetramers and the hexamers under the conditions of their measurements. As the conditions of our experiments were quite similar to theirs, the spectra corresponding to the class B compounds have to be considered as the sum of spectra of tetrameric and hexameric clusters of comparable intensity. Despite this, the $a_{1g}{}^{2-1}$ band has only one maximum in each case. Moreover, the width and the shape of this band are similar to those found in the tetramers' spectra. This can be explained only if the difference between the $a_{1g}{}^{2-1}$ ionization energies of tetramers and hexamers is less than or is of the same order as the half-width of the band (0.4 eV). This is in good agreement with the difference between the corresponding Koopmans' energies, which is 0.14 eV at the given level of theory.

In contrast with cluster size, dependence of the ionization energies on the inductive effect of the substituent is much more prominent. Changing the alkyl group from Et to *t*-Bu, the shift in both the first adiabatic and the vertical ionization energies of the $a_{1g}{}^{2-1}$ band is about 0.5 eV. This value is definitely larger than the change in the first vertical ionization energies of the corresponding alkyl alcohols (~0.4 eV), thiols (~0.3 eV), amines (~0.2 eV), phosphines (~0.2 eV), and alkylhalogenides (Cl, Br, I: ~0.3 eV).[57] This observation is simply explained by the fact that in the case of alkyllithiums the electron is removed from an orbital with significant contribution from the α-carbon atom, while in the other cases the ionization energy corresponds to the lone pair of an adjacent atom.

D. Band Intensities and Jahn–Teller Distortion. According to the above interpretation of the PE spectra, the intensity ratio of the $t_{2g}{}^{6-1}$ and $a_{1g}{}^{2-1}$ bands of the tetramers is expected to be roughly 3:1. In contrast, experimentally it is found to be about 1:1. One of the possible origins of this discrepancy is the small ionization cross section of the $t_{2g}{}^{6-1}$ caused by large geometry change taking place during the ionization as a consequence of Jahn–Teller distortion of the ionic clusters and the change of the electrostatic interactions. To confirm this hypothesis, we have investigated the geometry of the ionic ground state of the clusters by ab initio quantum chemical calculations.

It can be shown by group theoretical considerations[58,59] that the subgroup geometries of a tetrahedral molecule accessible by Jahn–Teller distortion corresponds to either D_{2d} and D_2 coupled to vibrational modes of e symmetry or C_{3v}, C_{2v}, C_s, and C_1 coupled to vibrational normal modes of t_2 symmetry. Geometry optimizations were performed for $(MeLi)_4{}^+$ starting from all the possible symmetry subgroups, followed by second derivative calculations to determine whether the obtained stationary points correspond to minima. The obtained semiqualitative potential energy surfaces as a function of the distortion coordinate (ρ) of the neutral and the ionic tetrameric clusters are shown in Figure 5. According to the results of these UHF and UB3LYP

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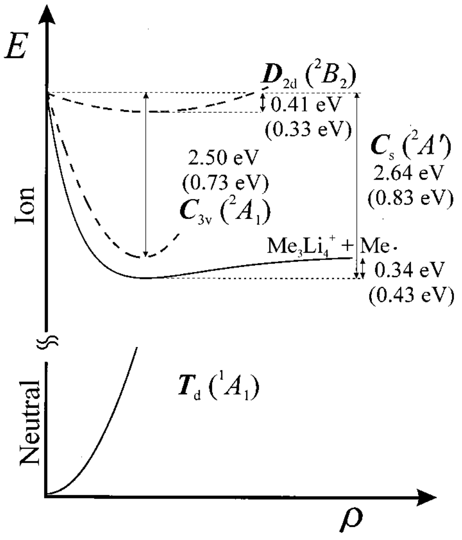

Figure 5. Qualitative configuration-coordinate diagram showing the Jahn–Teller distortion caused by electron ejection from a t_2 orbital of tetrameric alkyllithiums. (Numerical values obtained for MeLi at the UHF/6-31G** and (UB3LYP/6-31G**) levels of theory.)

Table 4. Extent of Jahn–Teller Distortion in $(MeLi)_4^+$ and $(MeLi)_6^+$ Clusters as Compared with the Undistorted Geometry of the Corresponding Neutral Clusters[a]

structure	Δr_{Li-Li}	Δr_{C-C}
$(MeLi)_4^+$ (C_s)	+0.007/+0.002	+0.035/+0.045
	+0.045/+0.042	+0.048/+0.055
	+0.622/+0.597	+0.492/+0.458
	+0.651/+0.630	+2.666/+2.646
$(MeLi)_6^+$ (C_{2h})[b]	+0.035/+0.014	−0.028/+0.039
	+0.407/+0.175	+0.464/+0.073
	−0.090/+0.008	−0.113/−0.047
	+0.237/+0.363	+0.075/+0.083

[a] All values are in Å, as obtained at the (R/U)HF/6-31G**/(R/U)B3LYP/6-31G** levels of theory. [b] Only distortion of the four shortest distances is reported. Values are sorted according to bond length.

calculations, the structure corresponding to the global minimum of the potential energy surface of the $(MeLi)_4^+$ cluster has C_s symmetry, and it is stabilized by 2.64 eV (UHF)/0.83 eV (UB3LYP) relative to the energy of the ionic cluster calculated at the geometry of the neutral species. Stationary points were also located with C_{3v} and D_{2d} symmetry restrictions. These structures, however, were found to be saddle points of different order. The geometry optimizations started from D_2 and C_{2v} symmetries did not yield new structures and resulted in the D_{2d} saddle point. Differences between the Li–Li as well as C–C distances (Table 4) in the neutral cluster and in the ionic structures are extremely large, which is responsible for the small ionization cross section as well as for the broadening of the t_{2g}^{6-1} band.

To arrive at the C_s minimum of the potential energy surface, the undistorted system has to be elongated along one of the C_3 axes, followed by a distortion symmetrical to one of the remaining mirror planes. Continuing the elongation of the cluster over the minimum, dissociation of $(MeLi)_4^+$ to $Me_3Li_4^+$ and to a methyl radical results. McLean et al.[38] have found that the dissociation energy of $(t\text{-}BuLi)_4^+$ is zero at least within their experimental error (0.25 eV). (According to their measurements, the appearance energy of $t\text{-}Bu_3Li_4^+$ and the ionization energy of $(t\text{-}BuLi)_4$ have the same value of 6.2 eV.) Our ab initio calculations, in good agreement with this, also predict low dissociation energy ({0.34/0.18} and {0.43/0.37} eV, determined at the UHF/6-31G** and UB3LYP/6-31G** levels of theory {without/with} zero-point energy correction, respectively) along this pathway. This low value and the huge distortion of ionic clusters are the consequences of the ionic character of the Li–C bond: if an electron is removed from an orbital mainly localized on the α-carbon, the electrostatic interaction between this atom and the surrounding lithium atoms vanishes. (According to Bickelhaupt et al.,[55] the a_{1g} orbital can be characterized as essentially a covalent bond, and the t_{2g} orbital as an ionic Li–C cluster bond.) In close correspondence to this, the peak of $Li_4R_3^+$ is one of the most intense ones (besides RLi_2^+) in the mass spectra of tetrameric alkyllitium compounds, indicating a preferred dissociation pathway. Thus, the appearance energy determination for $t\text{-}Bu_3Li_4^+$ of Vitkovskii et al.,[60] 8.1 eV, seems less accurate than that in McLean's work.[38] (The change of slope in the photoionization yield curve at 8.1 eV has been assigned to the dissociation of an autoionized molecule ion by the latter authors.)

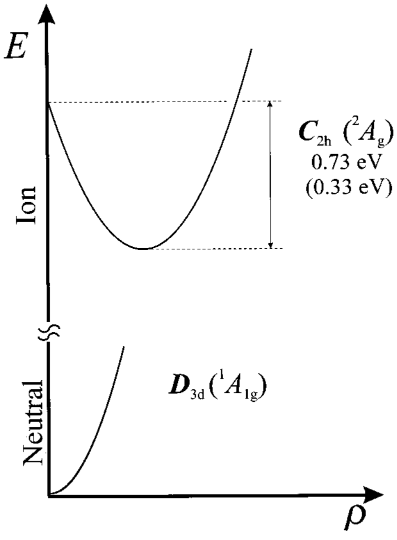

Figure 6. Qualitative configuration-coordinate diagram showing the Jahn–Teller distortion caused by electron ejection from an e orbital of hexameric alkyllithiums. (Numerical values obtained for MeLi at the UHF/6-31G** and (UB3LYP/6-31G**) levels of theory.)

The geometry of the ionic hexamers has also been investigated. The symmetry subgroups available by Jahn–Teller distortion of D_{3d} molecules are C_i and C_{2h}. Geometry optimizations both at UHF and at UB3LYP levels of theory resulted in a C_{2h} minimum (Figure 6). The extent of distortion (Table 4) is similarly large as in the case of tetramers, which explains the band shapes and intensities also in this case.

5. Concluding Remarks

Previous mass spectrometric investigations classified alkyllithium compounds according to their cluster size in the gas phase. The photoelectron spectroscopic in-

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(60) Vitkovskii, V. Yu.; Bravo-Zhivotovskii, D. A.; Pigarev, S. D.; Vyazankina, O. A.; Vyazankin, N. S. *J. Gen. Chem. USSR* **1985**, *56*, 853.

vestigations of this present study further support this classification. The mixture-like nature of class B compounds might be demonstrated by temperature-dependent measurements, using a double-chambered inlet probe, and the thermodynamics of this mixture might be examined further. Photoelectron spectra at our resolution also reveal that the ionization energies (the first ionization energy and the $a_{1g}{}^{2-1}$ band) of these compounds are basically determined by the alkyl group and they are unaffected by the cluster size. This observation suggests that the ionization potential of alkyl radicals adsorbed on the lithium surface should be quite close to the corresponding value obtained for the clusters. (This assumption might be verified by photoelectron spectroscopic investigation of a lithium surface treated by alkylhalogenides.) Using the mass-analyzed threshold ionization method, one could improve the resolution; furthermore the spectra of tetrameric and hexameric clusters could be separately studied. As this technique has proved itself[61] as a valuable tool for high-precision dissociation energy determinations, the appearance energy of fragment ions could also be given more accurately.

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[61] See, for example: Haines, S. R.; Dessent, C. E. H.; Müller-Dethlefs, K. *J. Chem. Phys.* **1999**, *111*, 1947.