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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · JANUARY 2009

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Journal:	<i>The Journal of Physical Chemistry</i>
Manuscript ID:	jp-2008-05264q
Manuscript Type:	Article
Date Submitted by the Author:	15-Jun-2008
Complete List of Authors:	Popov, Alexey; Moscow State University, Chemistry Dunsch, Lothar; IFW Dresden, Electrochemistry Senyavin, Vladimir; Moscow State University, Chemistry Department Trojanov, Sergey; Moscow State University, Department of Chemistry Burtsev, Alexander; Moscow State University, Chemistry Department



Spectroscopic and Theoretical Study of the Dimeric Dicationic Fullerene Complex, $[(C_{70})_2]^{2+}(Ti_3Cl_{13})^{-}_2$

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**RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required
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ABSTRACT: The first spectroscopic characterization of the dimeric dicationic fullerene complex $[(C_{70})_2]^{2+}(Ti_3Cl_{13})^{-}_2$ is reported and supported by DFT calculations. IR spectrum of the dimer is interpreted in terms of the normal modes of the pristine C_{70} , and the effects of charging C_{70} and the inter-cage bond formation between C_{70} units on the IR spectrum are discussed. Analysis of the vibrational spectrum of the anion, $Ti_3Cl_{13}^{-}$, is also provided. NIR absorption and fluorescence spectra of the complex are studied, and the dimer is shown to have a small HOMO-LUMO gap of 0.8 eV. Electronic structure of $[(C_{70})_2]^{2+}$ is studied with the use of DFT and compared to that of the other single-bonded fullerene dimers, including $[(C_{70})_2]^{2-}$, $(C_{69}N)_2$, and $[(C_{60})_2]^{2-}$. Characteristic features in the vibrational spectra and electronic structure of all single-bonded fullerene dimers are revealed.

KEYWORDS: fullerene dimer, DFT calculations, vibrational spectroscopy, spin density

Introduction

In a search for halogenation agents for fullerenes, we unexpectedly found that a mixture of Br_2 and TiCl_4 is an effective chlorinating system allowing preparation of new fullerene derivatives.¹ It was established that bromine concentration is critical to the composition of the reaction products.² For a reaction between C_{60} and TiCl_4 containing a high concentration of Br_2 , $\text{C}_{60}\text{X}_{24}$ ($\text{X} = \text{Cl}, \text{Br}$) products were obtained with Cl/Br ratio of 0.5 or higher. However, in the systems with lower Br_2 content, lower fullerene chlorides, C_{60}X_6 ($\text{X} = \text{Cl}, \text{Br}$) or dimeric $(\text{C}_{60}\text{Cl}_5)_2$, have been isolated and structurally characterized.² Recently, the mixture of TiCl_4 and Br_2 was successfully used for chlorination of C_{76} thus resulting in the first chloride of a higher fullerene, $\text{C}_{76}\text{Cl}_{18}$, investigated by single crystal X-ray crystallography.³

The system $\text{C}_{70} - \text{TiCl}_4 - \text{Br}_2$ provided further examples of new fullerene derivatives. At higher bromine concentration, a new chloride, $\text{C}_{70}\text{Cl}_{16}$, with unprecedented addition pattern was isolated and investigated by X-ray crystallography.¹ It was assumed that the presence of a strong Lewis acid (TiCl_4) in the system resulted in a generation of Br^+ or BrCl species that could act as halogenating agents under simultaneous (or subsequent) halogen exchange. An entirely unanticipated complex has been prepared in the same system at very low bromine content. A reaction of $\text{C}_{70}\text{Br}_{10}$ with excess TiCl_4 allowed the first isolation of an ionic complex, $[(\text{C}_{70})_2]^{2+}(\text{Ti}_3\text{Cl}_{13})_2^{-}$, containing a singly bonded dimeric dication, $[(\text{C}_{70})]^{2+}$ (Fig. 1), and trinuclear anion, $(\text{Ti}_3\text{Cl}_{13})^{-}$, both species having been observed for the first time.² It should be noted that cationic fullerenes are difficult to obtain due to high ionization potential of fullerene molecules. Thus, the oxidation $E_{1/2}$ potentials of C_{60} and C_{70} are as high as 1.26 and 1.20 V (vs. Fc/Fc^+), respectively.⁴ Known “all-carbon” cations were isolated as radical cations $[\text{C}_{60}^+]$ and $[\text{C}_{76}^+]$ in the salts with carborane anions $[\text{CB}_{11}\text{H}_6\text{X}_6]^{-}$ ($\text{X} = \text{Cl}, \text{Br}$) and investigated by means of EPR, IR, and NIR spectroscopies.⁴⁻⁶ Therefore, the isolation of cationic species of C_{70} under weakly oxidizing conditions, but rather due to a very high Lewis acidity of the media assisting the formation of stable anion, is quite remarkable. On the other hand, a formation of anionic fullerene species is favored by high electron affinities of both C_{60} and C_{70} . Therefore, both radical anions (C_{60}^- and C_{70}^-) in fullerides⁴ and

singly bonded anionic dimers, $[(C_{60})_2]^{2-}$ and $[(C_{70})_2]^{2-}$, can be isolated.⁷⁻¹¹ Significantly, as C_{70} has five inequivalent types of atoms, up to 15 different isomers of single-bonded $(C_{70})_2$ dimers are possible. However, only one isomer is found for $[(C_{70})_2]^{2+}$.² Moreover, also single but *different* isomer is found for $[(C_{70})_2]^{2-}$.⁹ At the same time, for $(C_{69}N)_2$, which is isoelectronic to $[(C_{70})_2]^{2-}$, four isomers were isolated,^{12,13} including those corresponding to the bonding motif of $[(C_{70})_2]^{2-}$, $[(C_{70})_2]^{2+}$ and their combination.^{14,15}

In this article we report on synthesis and spectroscopy of $[(C_{70})_2]^{2+}(Ti_3Cl_{13})_2^-$ and present a comparative theoretical study of singly bonded dimeric dicationic and dianionic $(C_{70})_2$ species as well as their heterofullerene analogue, $(C_{69}N)_2$.

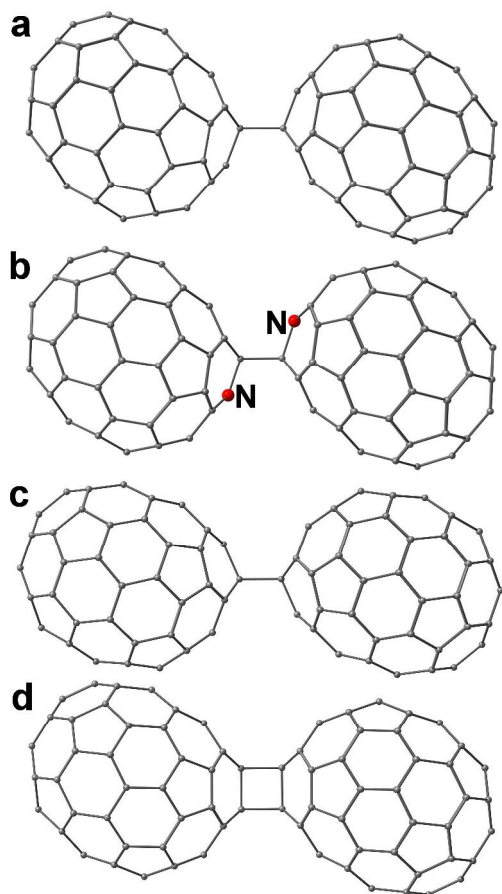


Figure 1. Molecular structures of (a) $[(C_{70})_2]^{2+}$, (b) isostructural $(C_{69}N)_2$, (c) $[(C_{70})_2]^{2-}$ and (d) neutrally charged $(C_{70})_2$.

Experimental Details

Synthetic route to $[(C_{70})_2]^{2+}(Ti_3Cl_{13})^-_2$ in this work was modified in that C_{70} fullerene was used instead of $C_{70}Br_{10}$ as described earlier.² 20 mg (0.023 mmol) C_{70} and 0.5-0.6 mL $TiCl_4$ were placed into glass ampoule. One drop of dry Br_2 (ca. 0.05 mL, 1.30 mmol) was added and the ampoule was evacuated and sealed. After heating the ampoule at ca. 100 °C for 2-3 d, black crystals were deposited on the ampoule's walls. They were separated from excess $TiCl_4$ by decanting and additionally dried in vacuo. Determination of unit cell for single crystals by X-ray crystallography confirmed the formation of $[(C_{70})_2]^{2+}(Ti_3Cl_{13})^-_2$ (triclinic unit cell parameters found in this work, $a = 10.192$, $b = 13.788$, $c = 16.713$ Å, $\alpha = 86.190$, $\beta = 89.034$, $\gamma = 79.508^\circ$, are very close to those reported for $[(C_{70})_2]^{2+}(Ti_3Cl_{13})^-_2$ in Ref. ²). Well crystallized compound placed under paraffin oil decomposes only slowly (15-20 min) in air atmosphere. A mixture of $[(C_{70})_2]^{2+}(Ti_3Cl_{13})^-_2$ and dry NaCl was pressed to pellet in a glove-box in argon atmosphere. The pellet was quickly transferred to the Equinox-55 FT-IR spectrometer (Bruker, Germany) just before recoding IR-NIR spectrum (370–7000 cm^{-1} range, resolution 1 cm^{-1} , 128 scans). The spectra taken within the first hour did not show noticeable changes. However at longer times decomposition of the complex became apparent, and only C_{70} absorption bands could be detected after exposure of the pellet in air for 24 hours. For recording Raman and luminescence spectrum, crystals of $[(C_{70})_2]^{2+}(Ti_3Cl_{13})^-_2$ were placed into thin-walled capillaries which were then sealed off immediately after taking them out of the glove-box. The spectra were measured with FRA-106 Raman module attached to Equinox-55 FT-IR spectrometer (excitation with 1064 nm line of Nd-YAG laser) and Jobin Yvon T 64000 triple spectrometer (excitation with 514.5 nm line of Ar^+ laser).

Computational Details

Optimization of geometry parameters and hessian calculations was performed using PBE functional¹⁶ and TZ2P-quality basis set with {6,3,2}/(11s,6p,2d) contraction scheme implemented in the PRIRODA package.^{17,18} The code employed expansion of the electron density in an auxiliary basis set to accelerate evaluation of the Coulomb and exchange-correlation terms.¹⁷

Results and Discussion

Vibrational spectroscopy. Vibrational spectra of C_{70} were thoroughly studied by several groups, and their interpretation based on DFT calculations was provided.^{19,20} As C_{70} has rather high D_{5h} symmetry, limited number of its fundamentals is IR-active (21 E' + 10 A_2'' symmetry types), and though this number is much larger than in C_{60} , the spectra of C_{70} are still rather simple because only few IR-active bands have high intensity (Figure 2). Charging of the fullerene and formation of the inter-cage bond(s) inevitably results in the lowering of the symmetry, and hence the spectra of the dimer should be much more complex. The monomeric C_{70} unit in C_{2h} -symmetric $[(C_{70})_2]^{2+}$ dimer retains only C_s site symmetry. Therefore, vibrational modes of the C_{70} units are transformed to A' and A'' symmetry types, and in the dimer these vibrations transform to $104A_g + 100B_g + 100A_u + 104B_u$ modes (see Table 1 for correlation of irreducible representation). Thus, all fundamentals of C_{70} lose their degeneracy and should produce IR and Raman active vibrations in the spectra of the dimer. The same symmetry situation is applied to the neutral $(C_{70})_2$, which also has C_{2h} symmetry,²¹ and its spectra indeed were shown to be more complicated than those of the monomer. Formation of the inter-cage bond can also produce specific localized vibrations. Finally, charging the cage modifies its electronic structure, the effect which can also reflect itself in the vibrational spectra. These issues are analyzed in detail in the following part of this section.

Figure 2 shows the IR spectrum of the $[(C_{70})_2]^{2+}(Ti_3Cl_{13})^-_2$ complex as compared to the spectrum of C_{70} and to the DFT-computed spectrum of the $[(C_{70})_2]^{2+}$ dimer. By the virtue of comparably high mass of Ti and Cl atoms, absorption bands of the anion occur at low frequencies (below 450 cm^{-1} , see further discussion) and hence the spectrum in the medium-IR range can be attributed exclusively to the fullerene-based vibrations. Comparison to the spectrum of C_{70} has shown that partial decomposition of the complex still took place, most probably initiated by the traces of water in NaCl used for the pellet formation. The bands which coincide in frequency to those of C_{70} and hence can be attributed to the parent fullerene are denoted by arrows in Fig. 2 (note that the dimer may also have vibrational frequencies with the same wavenumbers). However, as the spectrum of C_{70} is substantially less rich,

vibrational features of the cationic dimer can be determined unambiguously. Calculated spectrum for $(C_{70})_2^{2+}$ provides reasonable agreement with the experimental data, and hence can be used as a base for the detailed analysis.

Raman spectroscopic studies of the complex met sever difficulties due to the high fluorescence background and/or low sample stability under laser irradiation. Thus, the use of the infrared laser ($\lambda_{\text{ex}}=1064$ nm) for the excitation of the spectra resulted only in the luminescence background, which prevented the measurement of the Raman spectrum. When 514 nm line of Ar^+ laser was used, the sample was found to be unstable at the medium laser power, and only when very low laser power (0.07 mW) was applied, the sample exhibited long-term stability and afforded the measurement of the Raman spectrum (however, due to the low intensity of the excitation laser, the signal-to-noise ratio is rather small). The spectrum was found to be very similar to the spectrum of C_{70} measured with the same excitation wavelengths, the only noticeable differences being additional features in $1300\text{--}1500\text{ cm}^{-1}$ range and somewhat different intensity distribution. Dramatically different intensity distribution in the Raman spectrum of $[(C_{70})_2]^{2+}$ is predicted by DFT, which is not surprising because calculations predict non-resonant scattering intensities, while excitation of the spectrum in the visible range results in the preresonance scattering. Though the possibility of the dimer decomposition by the laser irradiation cannot be fully excluded, it should be noted that the Raman spectrum of $[(C_{70})_2]^{2-}$ in Rb-C_{70} system also showed close similarity to the spectrum of C_{70} , while inelastic scattering measurement clearly indicated the presence of the inter-cage bonds in that sample.²² However, in the view of the close similarity of the spectra of C_{70} and the dimer causing ambiguity in the interpretation of the Raman spectra, further discussion of the influence of dimerization and charging of C_{70} on the vibrational modes will be limited to the IR spectra and results of DFT calculations.

Table 1. Correlation of irreducible representation of D_{5h} , C_{2v} , C_s and C_{2h} groups.

D_{5h}	C_{2v}^a	C_s^b	C_{2h} (dimer)	IR ^c	Raman ^c
A_1'	A_1	A'	A_g+B_u	$0 \rightarrow 1$	$1 \rightarrow 1$
A_2'	B_1	A''	A_u+B_g	$0 \rightarrow 1$	$0 \rightarrow 1$
E_1'	A_1+B_1	$A'+A''$	$A_g+B_g+A_u+B_u$	$1 \rightarrow 2$	$0 \rightarrow 2$
E_2'	A_1+B_1	$A'+A''$	$A_g+B_g+A_u+B_u$	$0 \rightarrow 2$	$1 \rightarrow 2$
A_1''	A_2	A''	A_u+B_g	$0 \rightarrow 1$	$0 \rightarrow 1$
A_2''	B_2	A'	A_g+B_u	$1 \rightarrow 1$	$0 \rightarrow 1$
E_1''	A_2+B_2	$A'+A''$	$A_g+B_g+A_u+B_u$	$0 \rightarrow 2$	$1 \rightarrow 2$
E_2''	A_2+B_2	$A'+A''$	$A_g+B_g+A_u+B_u$	$0 \rightarrow 2$	$0 \rightarrow 2$

^a the symmetry of C_{70}^{+} ; ^b cite-symmetry of C_{70} in $[(C_{70})_2]^{2+}$; ^c two last columns show activation and splitting pattern for C_{70} modes in $[(C_{70})_2]^{2+}$.

Table 2. PBE/TZ2P computed inter-cage bondlengths (Å), the frequencies of characteristic vibrations of single-bonded dimers (cm^{-1}) and dimerization energy (kJ mol^{-1}).

	inter-cage bond, Å	"translation", A_g		intercage, B_u		stretch, A_g	E_{dim} , kJ mol^{-1}
		exp	calc ^a	exp	calc ^a	calc ^a	
$[(C_{70})_2]^{2+}$	1.647		64	833	846, 850	843	100.6
$[(C_{70})_2]^{2-}$	1.634		65	800, 842 ^c	831, 866	876, 897	95.7
a,a-($C_{69}N$) ₂	1.593		68		822, 865	983	-142.7
b,b-($C_{69}N$) ₂	1.597		66	823 ^d	834, 910	977	-111.9
$[(C_{60})_2]^{2-}$	1.653	82 ^b	69	816, 838 ^e	845, 860	858	137.3
($C_{59}N$) ₂	1.596	88 ^b	74	844 ^f	840, 857	931, 992	-118.2

^a all calculated values in the Table are obtained in this work at the PBE/TZ2P level; ^b Ref. 24; ^c Refs. 9, 28; ^d Ref. 14; ^e Ref. 27; ^f Ref. 26.

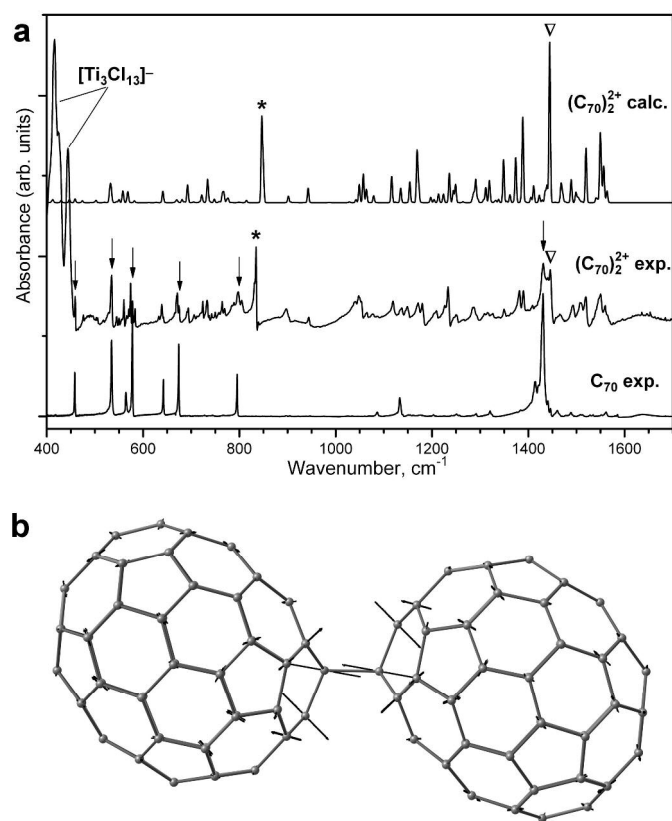


Figure 2. (a) Experimental and calculated IR spectra of $[(C_{70})_2]^{2+}$ and experimental IR spectrum of C_{70} ; (b) displacement pattern for characteristic IR mode of the inter-cage bond at 835 cm^{-1}

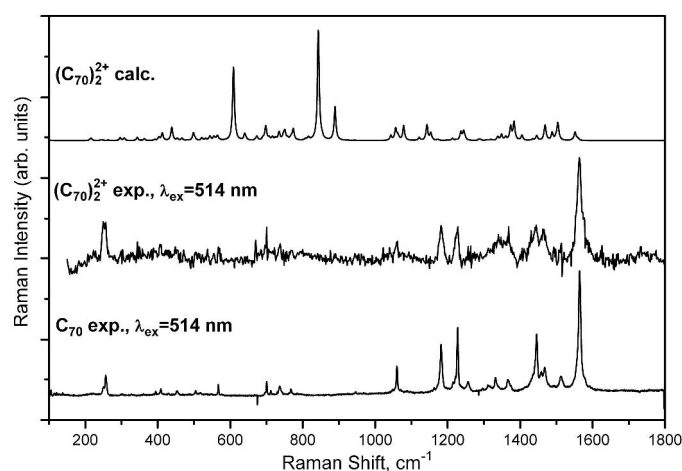


Figure 3. Experimental Raman spectrum $[(C_{70})_2]^{2+}(Ti_3Cl_{13})_2^-$, compared to the Raman spectrum of C_{70} ($\lambda_{ex}=514$ nm) and DFT-computed Raman spectrum of $[(C_{70})_2]^{2+}$.

Formation of the inter-cage bond forces some of the "external" degrees of freedom (translational and rotational) of the monomers to become vibrations of the dimer molecule. Such vibrations usually have low frequency (less than 150 cm^{-1}), and for the neutrally charged dimers of C_{60} and C_{70} as well as for $[(\text{C}_{60})_2]^{2-}$ some of them could be observed in the Raman spectra.^{21,23,24} Unfortunately it was not possible to measure Raman spectrum of $[(\text{C}_{70})_2]^{2+}$ in this range because of the strong background level, and so we will discuss this kind of vibrations only from the theoretical point of view. As anticipated, DFT calculations predict six low frequency (below 100 cm^{-1}) vibrations of the dimer originating from the frustrated rotations and translations of the monomer units. The modes with purely rotational character occur at $8\text{ (A}_u)$, $17\text{ (A}_u)$, and $19\text{ (B}_u)\text{ cm}^{-1}$, the stretching inter-cage mode is predicted at $64\text{ cm}^{-1}\text{ (A}_g)$, and two modes with the mixed translational-rotational character are predicted at $81\text{ (B}_g)$ and $86\text{ cm}^{-1}\text{ (A}_g)$. The modes with similar low frequencies are found for all single-bonded dimers considered in this work (see Table 2). The frequencies of these vibrations are systematically lower than predicted at the same level of theory for the neutrally charged $(\text{C}_{70})_2$, which can be readily explained the stronger inter-cage linkage by two covalent bonds in $(\text{C}_{70})_2$. For the latter, cage "librations" occur at $18\text{ (A}_u)$, $21\text{ (A}_u)$, and $29\text{ cm}^{-1}\text{ (B}_u)$, A_g "stretching" mode is predicted at 80 cm^{-1} , and mixed translational-rotational vibrations occur at $114\text{ (B}_g)$ and $127\text{ (A}_g)$. Three latter modes can be identified in the experimental spectrum of $(\text{C}_{70})_2$ at 89 , 117 and 129 cm^{-1} ,²¹ respectively, in close agreement with DFT-computed values.

In the mid-IR range, specific vibration located presumably at the inter-cage bond and the neighboring carbon atoms is found as a strong band at 833 cm^{-1} (846 cm^{-1} calc., B_u symmetry type). Its atomic displacement pattern is visualized on Figure 2; this mode can be roughly described as a translational displacement of the inter-cage bond as a whole accompanied by the radial motions of the neighboring carbon atoms. Analysis of the IR spectra of single-bonded fullerene dimers available in the literature as well as DFT calculations performed in this work have shown that vibrations of this sort are found for all single-bonded fullerene dimers in $800\text{--}900\text{ cm}^{-1}$ range (see Table 2), and these modes always have high IR intensity. Note that usually this mode is partially mixed with cage vibrations and has considerable contribution in two-three vibrations of the dimers. Earlier Andreoni et al.²⁵ predicted that such

vibrations should appear in the spectrum of $(C_{59}N)_2$ at 850 cm^{-1} , and later they were indeed observed by Krause et al as a multiplet of lines at $819/836/844\text{ cm}^{-1}$ with the strongest band at 844 cm^{-1} .²⁶ In the IR spectrum of the quenched Rb- C_{60} phase²⁷ comprising of $[(C_{60})_2]^{2-}$ dimers this mode can be attributed to the bands at 816 and 838 cm^{-1} , while in the IR spectra of $[(C_{70})_2]^{2-}$ we assign this mode to the strong band at 800 cm^{-1} and, with less confidence, to the medium intensity band at 842 cm^{-1} .^{9,28} Finally, in the spectrum of b,b- $(C_{69}N)_2$ this mode is probably responsible for a band at 823 cm^{-1} .¹⁴ In summary, "translational" mode of the inter-cage bond in single-bonded dimers always appears in $800\text{--}900\text{ cm}^{-1}$ range with high IR intensity and can be used as IR fingerprint of single-bond fullerene dimers (Table 2).

In terms of the monomeric unit, this characteristic vibration of the inter-cage bond can be described as a radial displacement of the four-coordinated carbon atom. Given displacement in two monomeric units occur in anti-phase, resultant vibration of the dimer is IR active and can be described as translation of the inter-cage bond as a whole as discussed above. On the contrary, if displacements in two monomeric units are in phase, resultant vibration can be described as A_g -symmetric stretching mode of the inter-cage bond (note that opposed to the lower-frequency inter-cage stretching mode described above, here centers of mass of the monomeric units remain static). The later is Raman active and expected at somewhat higher frequency than the "translational" mode (Table 2). Unfortunately, we could not identify this mode either in our spectrum or in the literature Raman spectra of $[(C_{60})_2]^{2-}$ and $(C_{59}N)_2$, presumably because of its low intensity.

To estimate the effect of the cage charging on the vibrational spectra, first we have computed the spectra of C_{70}^+ cation. Unfortunately, experimental data on this ion are not available, and this discussion is inevitably limited to the computational results. As HOMO of C_{70} is two-fold degenerated, removing one electron from this orbital results in the Jahn-Teller distortion of the cation with the symmetry reduction from D_{5h} to C_{2v} . Indeed, optimization of the coordinates of C_{70}^+ without any symmetry constraints resulted in C_{2v} symmetric structure for the cation. Figure 4 shows DFT-optimized bondlengths in C_{70}^+ as compared to those in C_{70} calculated at the same level of theory. As can be seen, the bondlengths in the cation are very close to those in the pristine C_{70} , the difference not exceeding 0.01

Å and in most cases being much smaller. In C_{2v} symmetry, degeneracy of C_{70} vibrations is lifted and therefore a splitting and mixing of the parent C_{70} modes can happen (see Table 1 for correlation between irreducible representations of D_{5h} and C_{2v} groups). Projecting vibrational eigenvectors of C_{70}^+ on the space of the vibrational eigenvectors of C_{70} has shown that the mixing is rather weak, and with the few exceptions, vibrational forms of C_{70} are mostly preserved in the cation. This is a sensible result taking into account small structural changes in C_{70} induced by removal of one electron. The splitting of E -type modes of C_{70} is also quite small, usually less than 10 cm^{-1} , however in some cases the larger values are observed. The highest degree of splitting is found for the $E_1'(13)$ mode of C_{70} (calc. 1082 cm^{-1} , exp. 1087 cm^{-1}), which is split into 990 cm^{-1} (B_2) and 1088 cm^{-1} (A_1) modes in the cation. This vibration can be described as stretching mode of the longest C–C bonds at the equator of C_{70} (Fig. 2). The other C_{70} vibrations with considerable degree of splitting in the cation are: $E_1'(2)$ (calc. 360 cm^{-1} , exp. 361 cm^{-1}) $\rightarrow 332\text{ cm}^{-1}$ (B_2) + 359 cm^{-1} (A_1); $E_1''(11)$ (calc. 1057 , exp. 1048) $\rightarrow 1027\text{ cm}^{-1}$ (B_1) + 1058 cm^{-1} (A_2); $E_1'(14)$ (calc. 1174 , exp. 1176) $\rightarrow 1146\text{ cm}^{-1}$ (B_2) + 1168 cm^{-1} (A_1); $E_1'(20)$ (calc. 1475 , exp. 1489) $\rightarrow 1450\text{ cm}^{-1}$ (B_2) + 1482 cm^{-1} (A_1); $E_1'(21)$ (calc. 1552 , exp. 1557) $\rightarrow 1526\text{ cm}^{-1}$ (B_2) + 1559 cm^{-1} (A_1). The special case of splitting is $E_2'(1)$ mode of C_{70} (calc. 219 , exp. 225), which is largely responsible for the Jahn-Teller distortion of the cage in C_{70}^+ . In the cation the frequency of one of its components is only 19 cm^{-1} (B_2), while another component occurs at the frequency of 214 cm^{-1} (A_1). As can be seen, in all E -symmetry modes subjected to considerable splitting upon charging of C_{70} , A_1 (A_2) component retains the frequency of the parent C_{70} mode, while B_2 (B_1) component is red-shifted.

We could not find any systematic shift in vibrational frequencies of the cation. For some modes, the frequencies are larger than in C_{70} , for others they are smaller, and there is no correlation between the shift and the range (see Table S2 in Supporting Information). For majority of modes, vibrational frequencies in the cation lie within 10 cm^{-1} of the corresponding frequencies in C_{70} . This can be compared to the experimental data on C_{76}^+ and C_{76} , for which the shift of vibrational frequencies also did not exceed 8 cm^{-1} .⁶

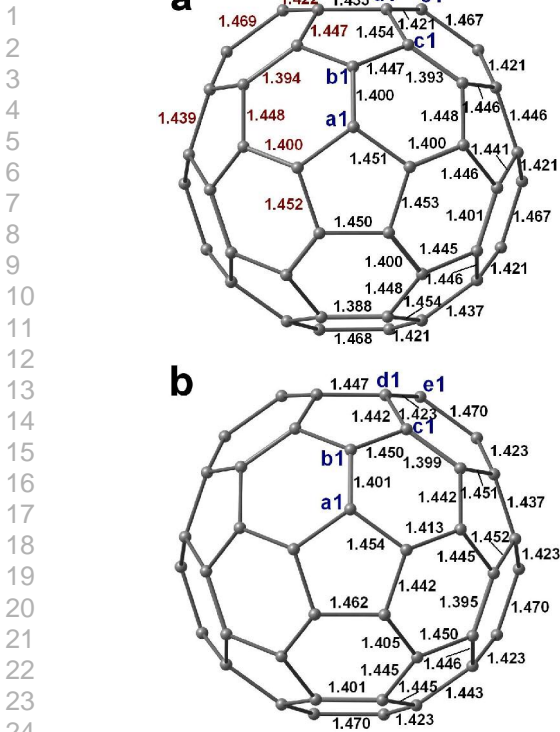


Figure 4. DFT-optimized bondlengths and atom numbering in C₇₀⁺ (a) and C₇₀⁻ (b). The bondlengths in C₇₀ optimized at the same level of theory are also shown in (a) highlighted with brown.

Table 3. Experimental and selected^a calculated vibrational frequencies and infrared intensities in [(C₇₀)₂]²⁺ and normal mode assignment.

sym	calc		exp		assignment in terms of C ₇₀ modes {exp/calc, cm ⁻¹ }, % ^d
	v, cm ⁻¹	Int, % ^b	v, cm ⁻¹	Int ^c	
B _u	458.6	2.34	458	w, C ₇₀	92 A ₂ "(2) {458 /457}
B _u	473.7	1.15	476	w	94 E ₁ "(3) {480/476}
B _u	530.4	5.37	535	m, C ₇₀	66 E ₁ (5) {534/533}, 16 E ₂ "(4) {-/518}, 14 E ₂ '(5) {536/537}
A _u	532.3	6.34	535	m, C ₇₀	78 E ₁ (5) {534/533}, 14 E ₂ '(5) {536/537}
B _u	533.8	4.11	535	m, C ₇₀	70 E ₂ '(5) {536/537}
A _u	534.6	1.21	535	m, C ₇₀	82 E ₂ '(5) {536/537}
A _u	544.8	0.63	545	w	88 E ₁ "(5) {549/550}
B _u	549.8	1.91	550	w	72 E ₁ "(5) {549/550}
B _u	557.6	5.91	560	w+	54 A ₁ '(4) {568/563}, 38 E ₂ "(5) {557/559}
B _u	558.8	2.01	560	w+	52 E ₂ "(5) {557/559}, 24 A ₁ '(4) {568/563}, 16 A ₂ '(3) {564/563}
B _u	567.2	2.78	574	m	72 A ₂ '(3) {564/563}, 14 E ₁ (6) {578/573}
A _u	568.7	4.96	574	m	96 E ₁ (6) {578/573}
B _u	581.7	1.16	583	w	76 E ₁ (6) {578/573}
B _u	640.9	5.82	639	w+	94 E ₁ (7) {642/643}
B _u	669.6	1.62	672	m	78 E ₁ (8) {674/670}

sym	calc		exp		assignment in terms of C ₇₀ modes {exp/calc, cm ⁻¹ }, % ^d
	v, cm ⁻¹	Int, % ^b	v, cm ⁻¹	Int ^c	
B _u	692.2	11.36	694	w+	82 A ₂ '(4) {695/694}
B _u	704.5	0.37	706	w	92 E ₂ "(7) {702/704}
B _u	721.6	4.83	724	w+	78 E ₁ "(7) {713/718}
B _u	733.7	12.96	733	w+	46 E ₁ (9) {728/732}, 36 E ₂ '(8) {727/734}
B _u	747.8	2.12	750	w	42 E ₂ '(9) {737/737}, 18 E ₁ "(8) {760/758}, 16 E ₁ (10) {795/746}
B _u	764.5	5.50	764	w+	44 E ₂ "(9) {765/763}, 26 E ₂ '(10) {750/751}, 18 E ₁ (10) {795/746}
B _u	767.5	6.00	764	w+	48 E ₁ "(9) {760/758}, 26 E ₂ '(11) {768/769}, 22 E ₂ '(10) {750/751}
B _u	776.5	2.51	769	w	86 E ₂ '(12) {773/784}
B _u	846.3	53.84	835	s	26 E ₁ (11) {835/854}, 18 E ₂ "(9) {765/763}, 18 E ₂ '(11) {768/769}
B _u	849.4	21.06	835	s	72 E ₁ (11) {835/854}
B _u	901.6	3.88	898	w+	78 E ₁ (12) {911/906}
B _u	942.4	8.57	944	w+	92 E ₂ '(13) {946/945}
B _u	1048.7	11.57	1040	w+	50 E ₂ '(14) {1070/1064}, 22 A ₁ '(7) {1060/1061}, 14 E ₁ "(11) {1048/1057}
B _u	1057.0	18.34	1048	m	38 E ₁ "(11) {1048/1057}, 32 E ₂ '(14) {1070/1064}, 20 A ₁ '(7) {1060/1061}
B _u	1063.5	8.59	1065	w	82 E ₂ "(12) {1076/1070}, 12 A ₁ '(7) {1060/1061}
B _u	1078.5	4.39	1077	w	82 E ₁ (13) {1087/1082}
B _u	1116.0	16.80	1119	m	70 A ₂ "(6) {1133/1130}
B _u	1134.7	9.19	1137	w+	22 A ₂ "(6) {1133/1130}, 22 E ₁ (14) {1176/1174}, 12 E ₂ "(13) {1152/1160}, 12 E ₂ '(15) {1196/1179}
B _u	1153.5	13.23	1149	w+	70 E ₂ "(13) {1152/1160}, 22 E ₁ (14) {1176/1174}
B _u	1168.7	32.36	1171	m	54 E ₂ '(15) {1196/1179}, 16 E ₁ "(12) {1172/1164}, 12 A ₁ '(8) {1182/1174}, 10 E ₁ (14) {1176/1174}
B _u	1171.9	11.04	1180	m	84 A ₁ '(8) {1182/1174}
B _u	1213.2	4.02	1209	w+	40 A ₂ "(7) {1203/1210}, 26 E ₁ "(13) {1222/1214}, 22 A ₂ '(7) {1215/1212}
B _u	1223.6	5.09	1226	w+	30 A ₁ '(9) {1227/1227}, 22 E ₁ (15) {1251/1243}, 12 E ₁ "(13) {1222/1214}, 12 E ₂ '(16) {1258/1253}
B _u	1235.6	18.80	1233	ms	50 A ₁ '(9) {1227/1227}, 44 E ₁ (15) {1251/1253}
B _u	1243.9	7.68	1245	w+, br	70 E ₂ "(14) {1248/1246}, 24 E ₂ '(16) {1258/1253}
B _u	1248.6	11.70	1250	w+, br	30 E ₂ '(16) {1258/1253}, 26 E ₁ (15) {1251/1243}, 14 A ₁ '(9) {1227/1227}
A _u	1283.6	2.37	1287	m, br	60 E ₁ "(14) {1296/1294}
B _u	1286.5	5.97	1287	m, br	42 E ₁ "(14) {1296/1294}, 34 E ₁ (16) {1291/1292}
B _u	1290.4	14.76	1287	m, br	44 E ₁ (16) {1291/1292}, 44 E ₁ "(14) {1296/1294}
B _u	1311.3	9.51	1315	w	50 E ₂ "(15) {1302/1311}, 22 E ₂ '(17) {1332/1324}
B _u	1318.7	12.94	1326	w	66 E ₁ (17) {1320/1320}, 24 E ₁ "(15) {1310/1318}
B _u	1348.2	27.51	1350	w+	78 E ₂ '(18) {1348/1345}
B _u	1373.4	25.92	1381	m	82 E ₂ '(19) {1374/1356}
B _u	1388.2	54.49	1390	m	52 E ₂ "(17) {1400/1393}
A _u	1410.7	10.75	1409	w	44 E ₁ (18) {1414/1406}, 26 E ₁ (19) {1489/1475}, 12 E ₁ "(17) {1435/1429}
B _u	1444.0	100.00	1446	s	84 E ₂ "(18) {1455/1446}
B _u	1467.4	10.19	1465	w, br	58 A ₁ '(11) {1467/1467}, 12 E ₁ (19) {1430/1430}
B _u	1469.3	4.13	1465	w, br	76 E ₁ (20) {1489/1475}
B _u	1471.3	3.91	1465	w, br	42 A ₂ "(9) {1460/1463}, 16 E ₁ (20) {1489/1475}, 10 A ₁ '(11) {1467/1467}
B _u	1488.6	13.88	1493	m	44 E ₂ '(20) {1500/1491}, 28 A ₂ "(9) {1460/1463}, 20 A ₁ '(11) {1467/1467}

sym	calc		exp		assignment in terms of C ₇₀ modes {exp/calc, cm ⁻¹ }, % ^d
	v, cm ⁻¹	Int, % ^b	v, cm ⁻¹	Int ^c	
B _u	1498.3	6.31	1507	m	30 E ₂ '(20) {1500/1491}, 22 E ₁ "(18) {1511/1503}, 12 E ₂ "(21) {1520/1510}
B _u	1519.4	34.98	1519	ms	18 E ₂ '(21) {1520/1510}, 18 E ₁ (21) {1557/1552}, 16 E ₂ "(20) {-/1556}, 14 E ₁ "(18) {1511/1503}, E ₂ '(22) {1545/1555}
B _u	1548.9	42.59	1550	ms	32 E ₁ (21) {1557/1552}, 32 A ₁ '(12) {1564/1559}, 20 A ₂ "(10) {1563/1553}
B _u	1556.2	23.14	1560	m	54 A ₁ '(12) {1564/1559}, 28 A ₂ "(10) {1563/1553}, 10 E ₁ "(19) {1564/1557}
A _u	1563.3	6.47	sh		56 E ₂ '(22) {1545/1555}, 14 E ₂ "(20) {-/1556}, 12 E ₁ "(19) {1564/1557}

^a full list of calculated frequencies of the dimer is given in Supporting Information, Table S1;

^b Calculated IR intensities are in %, 100% is B_u mode at 1444 cm⁻¹ (calc);

^c experimental intensities are w (weak) < w+ < m (medium) < ms (medium-strong) < s (strong), br – broad, "C₇₀" marks the modes which frequencies coincide with C₇₀ modes and hence their assignment to the dimer is somewhat ambiguous;

^d assignment in terms of C₇₀ normal modes results from projection analysis, % of C₇₀ vibration is given for each vibration of the dimer (contributions less than 10 % are omitted), for C₇₀ modes the values in brackets are experimental/calculated frequencies, the full list of C₇₀ vibrational frequencies is given in Supporting Information, Table S2.

As to the IR spectrum of [(C₇₀)₂]²⁺, projection analysis has shown that the most intense bands of the dimer originate either from IR or, in rare cases, from Raman-active modes of C₇₀ (Table 3). In particular, majority of intense IR modes of C₇₀ have counterpart in the spectrum of [(C₇₀)₂]²⁺ with medium to strong intensity. In the dimer the frequencies of C₇₀ modes are almost the same, shifting normally to the higher frequencies by 2–6 cm⁻¹. However, there are two important exclusions from these relations. The first one is E₁'(10) mode of C₇₀ at 795 cm⁻¹, which can be described as out-of-plane vibrations of benzene rings on the equator of C₇₀ molecule. There is no intense counterpart for this mode in the spectrum of [(C₇₀)₂]²⁺, and projection analysis has shown that this mode is strongly mixed with other C₇₀ vibrations. Its contributions are scattered over the 200 cm⁻¹ range in the spectrum of the dimer showing weak to negligible absorption intensities. Another exclusion is E₁'(19) at 1430 cm⁻¹, the strongest IR mode of C₇₀. Calculations showed that intensity of the corresponding vibrations in the dimer is very weak. Instead, the strong band at 1446 cm⁻¹ in the IR spectrum of [(C₇₀)₂]²⁺ is caused by the silent fundamental of C₇₀ E₂"(18), (calc. 1446, exp. 1455 cm⁻¹). Note that it would be impossible to

make this conclusion without projection analysis, and thus a wrong assignment of the dimer band at 1446 cm^{-1} to the $E_1'(19)$ mode of C_{70} could be proposed.

Vibrational Modes of $\text{Ti}_3\text{Cl}_{13}^-$. In addition to the cationic dimer of C_{70} , $[(C_{70})_2]^{2+}(\text{Ti}_3\text{Cl}_{13})^-_2$ also affords a new chlorotitanate anion, $\text{Ti}_3\text{Cl}_{13}^-$, which has never been observed in other Ti–Cl systems. This encouraged us to study its vibrational spectrum as well. Idealized symmetry of $\text{Ti}_3\text{Cl}_{13}^-$ is C_{3v} , its vibrations span $9A_1 + 5A_2 + 14E$ symmetry types, of which A_1 and E modes are IR-active. Figure 5 compares computed IR spectrum of $\text{Ti}_3\text{Cl}_{13}^-$ to the spectrum of the complex in the low frequency range. DFT predicts that the cluster vibrations occur in the range of $40\text{--}440\text{ cm}^{-1}$, and thus only a fraction of $\text{Ti}_3\text{Cl}_{13}^-$ modes is accessible experimentally. However, the most intense bands at 391 , 416 and 444 cm^{-1} are within the limits of our spectrometer and by comparison to the DFT-computed spectrum they can be readily assigned to the vibrational modes of the anion at 376 (E), 414 (E) and 435 cm^{-1} (A_1), respectively, whose vibrational displacement are shown in Figure 5 (note that IR intensities of the anion vibrations are several times higher than absorption intensities of the fullerene part). Analysis of the potential energy distribution has shown that these vibrations can be described as stretches of the terminal Ti–Cl bonds. Their averaged experimental bondlength is 2.208 Å ,² while theory yields 2.233 Å for Ti–Cl1 and 2.244 Å for Ti–Cl2 (see Figure 5 for the numbering of chlorine atoms). Bridging Ti– μ^2 -Cl3 bonds as well as Ti– μ^3 -Cl4 bonds are considerably longer (exp. 2.483 and 2.578 Å , calc. 2.512 and 2.655 Å , respectively), and their vibrations are expected at lower frequencies with the gap of 100 cm^{-1} (see Table S3). For instance, intense IR band at 271 cm^{-1} is largely due to the stretching vibration of Ti– μ^2 -Cl3 bonds. To our knowledge, no other Ti–Cl system except for the TiCl_4 and its complexes has been studied by vibrational spectroscopy.²⁹ In liquid TiCl_4 , IR-active stretching Ti–Cl mode is observed at 490 cm^{-1} (DFT yields 489 cm^{-1}), while in $\text{TiCl}_4\cdot 2\text{L}$ complexes (L=monodentate ligand) with hexacoordinated Ti this mode is shifted to ca 380 cm^{-1} reflecting elongation of Ti–Cl bondlengths with increase of Ti coordination number.²⁹ DFT-optimized Ti–Cl bondlength in TiCl_4 is 2.192 Å , while in the crystalline TiCl_4 the averaged Ti–Cl bond is 2.163 Å long. Thus, Ti–Cl bond in TiCl_4 is somewhat

shorter than terminal Ti–Cl bonds in $\text{Ti}_3\text{Cl}_{13}^-$ anion, in agreement with the higher Ti–Cl stretching frequency in TiCl_4 .

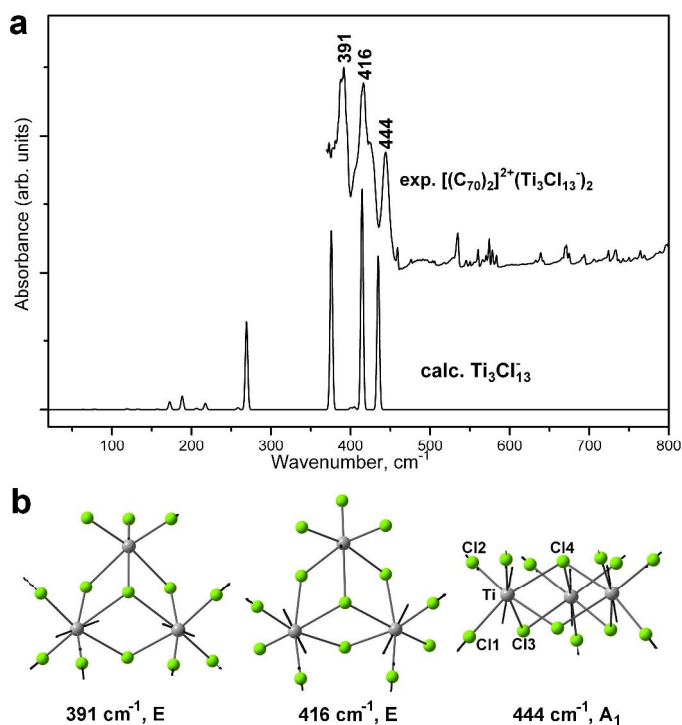


Figure 5. IR absorption spectrum of $[(\text{C}_{70})_2]^{2+}(\text{Ti}_3\text{Cl}_{13})_2^-$ in the low frequency range compared to the DFT-computed IR spectrum of $\text{Ti}_3\text{Cl}_{13}^-$ (a) and vibrational atomic displacements for the most intense IR modes of $\text{Ti}_3\text{Cl}_{13}^-$ (b).

Electronic structure of $[(\text{C}_{70})_2]^{2+}$ and other single-bonded dimers. Charged fullerenes, either in the anionic or cationic forms, exhibit characteristic absorptions in the near-infrared (NIR) range,⁴ which are attributed to $\text{SOMO} \rightarrow \text{LUMO} + \text{N}$ and $\text{HOMO} - \text{N} \rightarrow \text{SOMO}$ excitations, respectively. For instance, in C_{70}^- NIR band is observed at 1373 nm^4 and is assigned to the $\text{SOMO} \rightarrow \text{LUMO} + 4$ excitation.³⁰ The data on C_{70}^+ is more ambiguous largely because NIR bands are substantially less intense while the cation is very unstable. Bolskar observed absorption at $780 \text{ nm},^4$ and this observation agrees with the absorption spectrum of C_{70}^+ generated in neon matrix.³¹ Our time-dependent DFT calculations have shown that the band at 780 nm could be assigned to the $\text{HOMO} - 10 \rightarrow \text{SOMO}$ excitation predicted at 1.46 eV (851 nm), however calculations also predict more intense absorption at 0.76 eV (1641 nm) which was not observed

experimentally (see Supporting Information, Table S4). Dimerization of the ion-radicals should certainly affect NIR transitions. For instance, Konarev et al found two prominent NIR absorptions at 910 and 1240 nm in the spectrum of $[(C_{70})_2]^{2-}$ as opposed to one NIR band of C_{70}^- .³² To reveal the effect of the dimerization on the cation, we have studied the spectra of the complex in the NIR range. Figure 6 shows absorption spectrum of the sample (limited to the energy range of below 7000 cm^{-1}), superimposed on the luminescence spectrum excited with the 1064 nm line of Nd:YAG laser. In both spectra one can see the band at 0.9–0.8 eV, which may be assigned to the HOMO-LUMO transitions in $(C_{70})_2^{2+}$, and through the intercrossing of absorption and luminescence spectra, the band-gap of the dimer is estimated as 0.82 eV in reasonable agreement with the DFT-predicted value of 0.59 eV (note that DFT without exact exchange admixture usually underestimates HOMO-LUMO gap). DFT-predicted HOMO-LUMO gap of the $Ti_3Cl_{13}^-$ anion is 2.35 eV, and thus the NIR band is undoubtedly attributed to the dimeric fullerene cation.

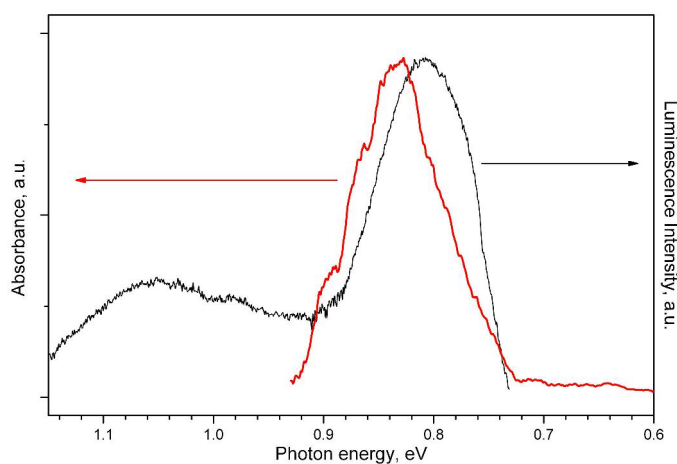


Figure 6. Absorption (red) and luminescence (black) spectra of $[(C_{70})_2]^{2+}(Ti_3Cl_{13})^-_2$ in the NIR range

To reveal the nature of NIR bands in single-bonded dimers of C_{70} we have analyzed their electronic structure in comparison to that of the radical anion and cation of C_{70} at the DFT level of theory. MO energy levels for the dimers are shown and compared to those of C_{70} on Figure 7 (note that the energy levels of charged species are shifted to the higher (cations) or lower (anions) energies to be seen on the same scale with C_{70}). One can see that in the radical anion and cation of C_{70} alpha and beta electrons

exhibit somewhat different energies while E -symmetry orbitals are split, but degree of splitting is rather small, and the structure of MO levels in both cation and anion is similar to that of C_{70} . However, electronic structure of the dimers is markedly different. They exhibit two specific MO levels which have no analogues in C_{70} and its radical anion or cation. In the anionic dimer these levels are occupied, while in the cationic dimer both are vacant. In the energy scale these levels are located in the middle of the HOMO-LUMO gap of C_{70} , and hence electron excitations to and from these levels are responsible for the NIR absorptions in $[(C_{70})_2]^{2+}$ and $[(C_{70})_2]^{2-}$, respectively. Figure 8 visualizes corresponding MOs of the dimers. Both MOs exhibit considerable degree of localization close to the inter-cage bond and can be described as symmetric and antisymmetric superposition of the same MO pattern of the monomeric unit. The orbital with symmetric superposition (A_g), which is LUMO+1 in $[(C_{70})_2]^{2+}$ and HOMO in $[(C_{70})_2]^{2-}$, has considerable bonding nature for the inter-cage bond, while "antisymmetric" orbital (B_u), which is LUMO in $[(C_{70})_2]^{2+}$ and HOMO-1 in $[(C_{70})_2]^{2-}$, has an anti-bonding character for this bond. Analysis of the spatial localization of other frontier orbitals in $[(C_{70})_2]^{2+}$ and $[(C_{70})_2]^{2-}$ have shown that they are largely reminiscent of C_{70} MOs.

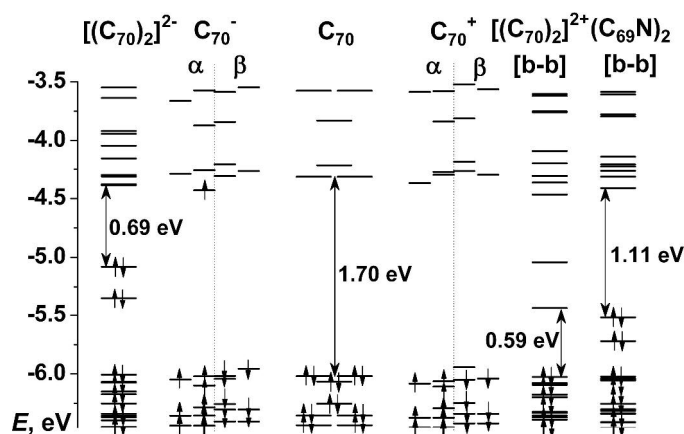


Figure 7. Frontier Kohn-Sham MO levels in single-bonded dimers, C_{70} and its ions. For the open shell structure, α and β spin levels are shown separately.

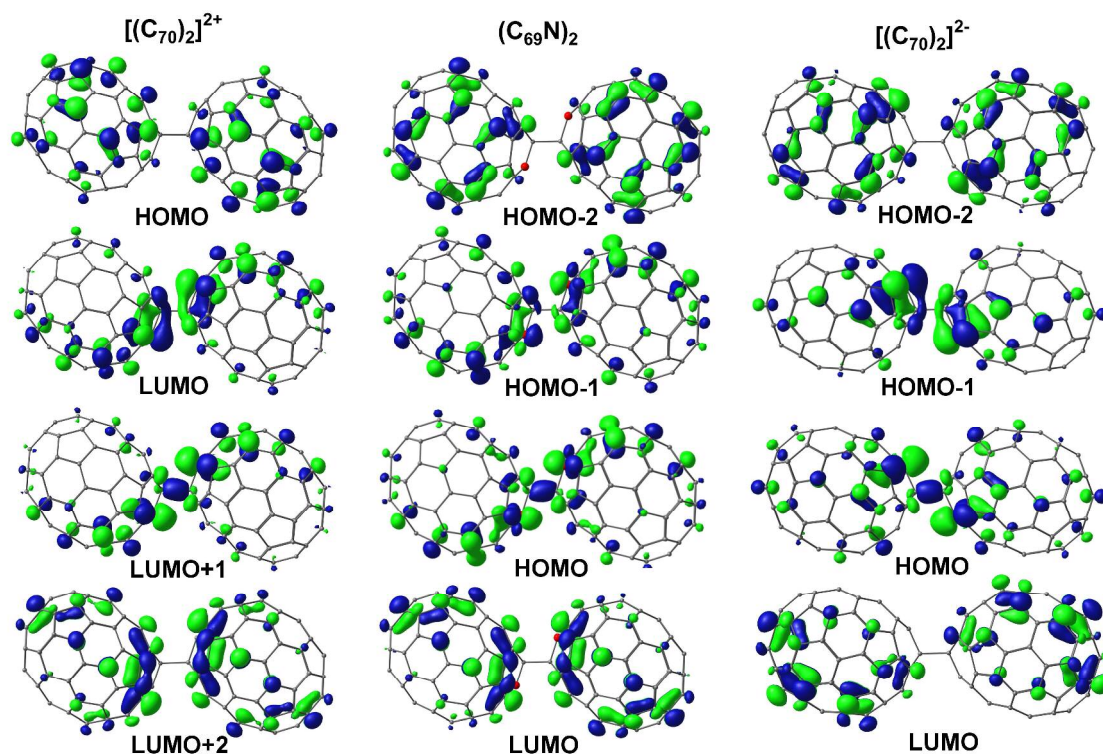


Figure 8. Frontier MOs in $[(C_{70})_2]^{2+}$ (left), isostructural $(C_{69}N)_2$ (middle), and $[(C_{70})_2]^{2-}$ (right).

Significantly, the shapes of characteristic MOs are almost the same in cationic and anionic dimers, even though they are linked through different carbon atoms. Moreover, the orbitals analogous to HOMO of $[(C_{70})_2]^{2-}$ and LUMO+1 of $[(C_{70})_2]^{2+}$ were earlier found in $[(C_{60})_2]^{2-}$ and $(C_{59}N)_2$.³³ The presence of two specific electronic levels in $[(C_{60})_2]^{2-}$ separated from all other orbitals was also confirmed by photoelectron spectroscopy,⁸ which showed a distinct two-band feature in the vicinity of the highest occupied orbitals. Thus, we conclude that such orbitals can be considered as a characteristic feature of all single-bonded dimers of fullerenes. It is also instructive to compare the electronic structure of the charged C_{70} dimers to that of $(C_{69}N)_2$. Though the shapes of characteristic orbitals in the latter is similar to that in $[(C_{70})_2]^{2+}$ and $[(C_{70})_2]^{2-}$ (Figure 8), HOMO and HOMO-1 in $(C_{69}N)_2$ are considerably stabilized (i.e. their energies are lowered with respect to the energies of all other orbitals). The same phenomenon was also observed for $(C_{59}N)_2$, both experimentally by photoelectron spectroscopy^{34,35} and theoretically by DFT calculations.³³ It can be attributed to the stabilizing effect of the additional positive charge on the nitrogen sites.

Structural Peculiarities of the Charged Dimers of C_{70} . C_{70} has five symmetry inequivalent atoms thus allowing a possibility of 15 different isomers of single-bonded dimers. Given five symmetry inequivalent atoms of C_{70} are labeled **a** to **e** from the top to the equator of the molecule (Fig. 4), experimentally available $[(C_{70})_2]^{2+}$ and $[(C_{70})_2]^{2-}$ isomers can be designated as $[\mathbf{a-a}]^{2+}$ and $[\mathbf{b-b}]^{2-}$, and this designation will be used in the following discussion. Note also that both **a** and **b** atoms are involved in the formation of the inter-cage bonds in the neutral $(C_{70})_2$ dimer.²¹ Our calculations have shown that the isomers with the opposite bond motifs, i.e. $[\mathbf{a-a}]^{2+}$ and $[\mathbf{b-b}]^{2-}$, are less stable than experimentally available structures $[\mathbf{b-b}]^{2+}$ and $[\mathbf{a-a}]^{2-}$ by 46.6 and 55.4 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. This shows that stability of single-bonded dimers can be substantially dependent on the bonding sites, and to get the deeper insight into this problem we have checked all possible bonding motifs for $[(C_{70})_2]^{2+}$ and $[(C_{70})_2]^{2-}$. Table 4 lists relative energies for all symmetric dimers (i.e., the dimers in which monomers are linked by the atoms of the same type). The energies of the “mixed” type dimers (e.g., $[\mathbf{a-b}]^{2+}$, etc.) were found to be well approximated by the mean value of the energies of two symmetric motifs (e.g., $\Delta E_{[\mathbf{a-b}]} \approx 0.5(\Delta E_{[\mathbf{a-a}]} + \Delta E_{[\mathbf{b-b}]})$ within 2–3 $\text{kJ}\cdot\text{mol}^{-1}$), and these values will not be discussed here in detail (see Table S5 in Supporting Information). It is remarkable that for both cationic and anionic dimers, experimental structures correspond to the lowest energy isomers. However, while $[\mathbf{a-a}]^{2-}$ isomer of the anionic dimer is substantially more stable than all other structures, $[\mathbf{d-d}]^{2+}$ isomer of dimeric dication is only 5.2 $\text{kJ}\cdot\text{mol}^{-1}$ less stable than experimentally determined structure of $[(C_{70})_2]^{2+}$. Furthermore, optimization of the mixed $[\mathbf{b-d}]^{2+}$ isomer revealed that it is only 2 $\text{kJ}\cdot\text{mol}^{-1}$ less stable than $[\mathbf{b-b}]^{2+}$ isomer.

Table 4. DFT relative energies (ΔE , $\text{kJ}\cdot\text{mol}^{-1}$) and inter-cage bondlengths ($d_{\text{C-C}}$, Å) in the isomers of $[(\text{C}_{70})_2]^{2+}$, $[(\text{C}_{70})_2]^{2-}$, and $(\text{C}_{69}\text{N})_2$ dimers.

	$[(\text{C}_{70})_2]^{2+}$		$[(\text{C}_{70})_2]^{2-}$		$(\text{C}_{69}\text{N})_2^{\text{a}}$		$\text{C}_{69}\text{N}^{\text{c}}$	
	ΔE	$d_{\text{C-C}}$	ΔE	$d_{\text{C-C}}$	ΔE	$d_{\text{C-C}}$	$\text{C}\rightarrow\text{N}^{\text{b}}$	ΔE
[a-a]	46.6	1.668	0.0	1.634	0.0	1.593	b	3.1
[b-b]	0.0	1.647	55.4	1.657	37.6	1.597	a	6.6
[c-c]	15.6	1.667	43.1	1.647	26.3	1.602	c	0.3
[d-d]	5.2	1.679	32.5	1.663	95.9	1.621	d	0.0
[e-e]	— ^d	— ^d	146.6	1.650	147.1	1.628	d	0.0
[2+2]	13.8		35.6					

^a in $(\text{C}_{69}\text{N})_2$ dimers [a-a] means that C_{69}N units are linked through C atoms of **a** type, just like for $(\text{C}_{70})_2$; ^b this column shows which carbon atom in C_{70} (closest to the C-sp^3 atom) is replaced by nitrogen; for [d-d] and [e-e] position of nitrogen is not obvious, and hence several isomer were computed and the values listed in the table correspond to the lowest energy isomers; ^c relative energies of C_{69}N radicals corresponding to the dimers; that is, the line [a-a] contains the data on the isomer of C_{69}N in which N replaces one of the carbon atoms of **b** type; ^d bonded state for the dimer was not found.

To shed the light on the reasons of such a strong dependence of the dimer stability on the bonding site, we have studied the structures of preceding radical-ions C_{70}^+ and C_{70}^- in more details. First, it is natural to consider that dimerization should occur through the sites with the highest spin density, and thus the spin density distribution in C_{70}^+ and C_{70}^- was analyzed. DFT-computed spin populations in these radical-ions are listed in Table 5, while spatial distribution of the spin density is shown in Figure 9. On the other hand, all fullerenes suffer inherit curvature-induced strain, and it is considered that the atoms with the highest curvature are most prone to the chemical modification.³⁶ A convenient measure of the local curvature (deviation from planarity) for a given carbon atom is provided by π -orbital axis vector (POAV) analysis.³⁷ In this approach, π -orbital vector is postulated to make equal angles, $\theta_{\sigma\pi}$, to three sigma bonds, and pyramidalization angle is defined as $(\theta_{\sigma\pi}-90^\circ)$. Larger $(\theta_{\sigma\pi}-90^\circ)$ values correspond to the higher curvature-induced strain. Table 6 lists $(\theta_{\sigma\pi}-90^\circ)$ values for C_{70} , C_{70}^+ and C_{70}^- . Note that cation and anion both have only C_{2v} symmetry due to Jan-Teller distortion.

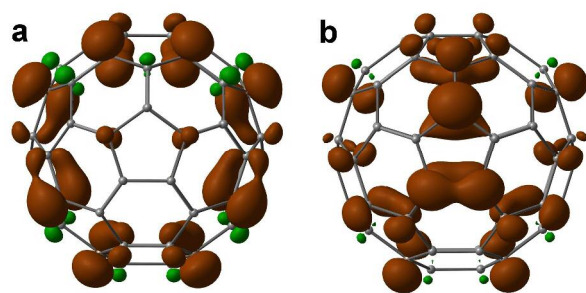


Figure 9. Spatial distribution of the spin density in C_{70}^+ (a) and C_{70}^- (b).

Table 5. Spin population in DFT-optimized structures of C_{70}^+ and C_{70}^- .

	C_{70}^+		C_{70}^-	
	per atom ^a	net ^b	per atom	net
a	-0.001, 0.014, 0.005	0.073	0.100, -0.011, 0.057	0.385
b	-0.023, 0.000, -0.014	-0.103	0.018, -0.001, 0.012	0.081
c	0.073, -0.026, 0.010, 0.070, 0.014	0.569	0.019, -0.008, 0.018, 0.035, -0.008	0.226
d	0.015, 0.071, 0.010, -0.022, 0.070	0.577	0.013, 0.046, 0.005, -0.015, 0.050	0.396
e	-0.005, -0.026, -0.007, 0.005, -0.023	-0.105	-0.005, -0.018, -0.006, 0.002, -0.017	-0.090

^a the values are listed in the order **a1**, **a2**, **a3** etc. Positions of **a1**, **b1**, etc. are shown in Fig. 4, other atoms of the same type are numbered in clock-wise direction; ^b the values summed up for all atoms of the given type.

Table 6. POAV pyramidalization angles ($\theta_{\sigma\pi}-90^\circ$) in DFT-optimized structures of C_{70} , C_{70}^+ and C_{70}^- .

	C_{70}	C_{70}^{+a}	C_{70}^{-a}
a	11.83	11.88, 11.75, 11.82	12.34, 11.56, 12.0
b	11.96	12.11, 12.07, 12.10	12.06, 11.81, 11.98
c	11.48	11.27, 11.67, 11.43, 11.20, 11.56	11.56, 11.28, 11.42, 11.60, 11.36
d	10.21	10.25, 9.96, 10.12, 10.31, 10.05	10.25, 10.38, 10.13, 10.05, 10.45
e	8.59	8.73, 8.70, 8.66, 8.68, 8.74	8.58, 8.51, 8.48, 8.51, 8.58

^a the values are listed in the order **a1**, **a2**, **a3** etc. Positions of **a1**, **b1**, etc. are shown in Fig. 4, other atoms of the same type are numbered in clock-wise direction

Analysis of the data in Tables 5 and 6 shows that the highest spin density in the monoanion is located on the **a1** atom, which is lying on the symmetry plane. The net spin population on **a** atoms is comparable to that of the atoms of **d**-type, however when the values for individual atoms are considered, spin population on **a1** is found to be twice or more times larger than on the other atoms. Moreover, **a1** atom also has the largest ($\theta_{\sigma\pi}-90^\circ$) value, 12.34° (for comparison, the value for the atoms of **a**-type in neutral C_{70} is 11.83°). Thus, dimerization of C_{70}^- through **a-a** bond formation is favored by both spin density and local curvature, which explains why $[\mathbf{a-a}]^{2-}$ is considerably more stable than all other isomer of $[(C_{70})_2]^{2-}$. The largest POAV values in the C_{70}^+ cation are found for the atoms of **b** type, and this is a probable explanation of the higher stability of $[\mathbf{b-b}]^{2+}$ dimer. However, the spin density distribution in the cation is substantially different than in the anion (Fig. 9) with the largest spin density corresponding to the atoms of **c** and **d** types. As a result, $[\mathbf{c-c}]^{2+}$ and $[\mathbf{d-d}]^{2+}$ isomers appear to be much closer in energy to $[\mathbf{b-b}]^{2+}$ than respective isomers of the anionic dimer.³⁸ Note that POAV analysis explains very low stability of $[\mathbf{e-e}]^{2-}$ dimer by small pyramidalization angle for **e** atoms (for the cationic dimer, this isomer did not provided a bounded state at all), which is in line with the avoidance of the **e** atoms in C_{70} and atoms at triple hexagon junctions in general in the chemical derivatization of higher fullerenes.³⁹⁻⁴¹ Finally, it is worth noting that the lowest energy isomers of $[(C_{70})_2]^{2+}$ and $[(C_{70})_2]^{2-}$ have the shortest DFT-optimized inter-cage bondlengths in each set of possible isomers.

It is instructive to compare the relative energies of $[(C_{70})_2]^{2-}$ isomers to those of the isoelectronic $(C_{69}N)_2$ dimer (Table 4). Similar to the $[(C_{70})_2]^{2-}$, $[\mathbf{a-a}]$ isomer is favored for $(C_{69}N)_2$ followed by $[\mathbf{c-c}]$ and $[\mathbf{b-b}]$, however the latter exhibit higher relative stability than for the anionic dimer (26.3 and $37.6 \text{ kJ}\cdot\text{mol}^{-1}$ vs 43.1 and $55.4 \text{ kJ}\cdot\text{mol}^{-1}$, respectively, see Table 4). In contrast to $[(C_{70})_2]^{2-}$ represented by the single $[\mathbf{a-a}]^{2-}$ isomer, three symmetric $[\mathbf{a-a}]$, $[\mathbf{b-b}]$,^{14,15} and $[\mathbf{c-c}]$ ¹³ isomers as well as mixed $[\mathbf{a-b}]$ isomer¹⁴ of $(C_{69}N)_2$ were isolated. In the similar synthetic conditions $[\mathbf{b-b}]$ is usually obtained in much higher yield, however, as follows from our results, it is only a kinetic product, and the relative yields of $(C_{69}N)_2$ isomers are largely determined by stability of the intermediates. Note that just like in

1 $[(C_{70})_2]^{2-}$, the shortest inter-cage C–C bond in $(C_{69}N)_2$ also corresponds to the most stable isomer.
2
3 However, the inter-cage bonds in the azafullerene dimers are systematically 0.04–0.06 Å shorter than in
4
5 the charged single-bonded dimers of C_{70} (Table 4). The same difference in the bondlengths was reported
6
7 for $(C_{59}N)_2$ and $[(C_{60})_2]^{2-}$ in Ref. ³³ (see also Table 4 for the results computed in this work).
8
9

10 **Binding energies.** The last column in Table 2 lists dimerization energies E_{dim} for the dimers (positive
11
12 value means that the dimer is unstable with respect to the decomposition into monomeric species). As
13
14 could be anticipated, both cationic and anionic dimers of C_{70} are significantly unstable (E_{dim} ca 100
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16 kJ/mol), which can be explained by a domination of Coulomb repulsion (E_{Coul}) in the inter-cage
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18 interactions,³³ and hence formation of the charged dimers is possible only in the presence of the counter-
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20 ions which compensate the strong Coulomb repulsion between the monomeric units. E_{Coul} can be
21
22 roughly estimated as a repulsion energy of two point charges located in the centers of mass of
23
24 monomeric units, which amounts to 136.3 kJ/mol for $[\mathbf{b-b}]^{2+}$. Probably more accurate estimation can
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26 be done by using Hirschfield atomic charges from DFT calculations and summing up all pair-wise inter-
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28 atomic interactions between different monomeric units. For $[\mathbf{b-b}]^{2+}$ this approach yields 146.6 kJ/mol,
29
30 and almost the same values within 3–4 kJ/mol are obtained for all other isomers of $[(C_{70})_2]^{2+}$ in spite of
31
32 the fact that they have different inter-cage distances. The latter can be explained by the fact that
33
34 distribution of excess charge in single-bonded dimers is mostly governed by the frontier orbitals
35
36 associated with the inter-cage bonds (see Fig. 8). As these orbitals have identical shapes in all isomers,
37
38 E_{Coul} computed by this method is almost the same for all isomers. Calculated values can be compared to
39
40 the experimentally measured Hubbard U value in $(C_{59}N)_2$ recently reported by Schulte et al.³⁵ U in
41
42 $(C_{69}N)_2$ can be interpreted as Coulomb repulsion in $[(C_{59}N)_2]^{2+}$ and is estimated as 106 kJ/mol for the
43
44 HOMO to 130 kJ/mol for the deeper lying orbitals.³⁵ Given E_{Coul} is subtracted from E_{dim} , the residue can
45
46 be interpreted as covalent contribution to E_{dim} , which turns to be negative. However, the values are still
47
48 much smaller than E_{dim} values predicted for $(C_{59}N)_2$ and $(C_{69}N)_2$, which can be explained by the longer
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50 inter-cage bonds in the charged dimers. Thus, Coulomb repulsion in the latter weakens covalent bonding
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52 between monomeric units.
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60

Note that computed E_{dim} reasonably correlates with the experimental data on decomposition of the dimers. The least stable dimer according to E_{dim} value, $[(C_{60})_2]^{2-}$, was shown to decompose at 160–250 K depending on the counter-ion,³² decomposition of $[(C_{70})_2]^{2-}$ occurs at 250–360 K,³² while for $(C_{59}N)_2$ substantial fraction of the dimer survived heating up to 750–830 K.^{26,42} Given similar kinetic stability is proposed for the $[(C_{70})_2]^{2-}$ and $[(C_{70})_2]^{2+}$ dimers, the synthesis of the latter at 373 K (the temperature used in this work) is most probably a reversible process, and hence thermodynamically stable **[b-b]**²⁺ isomer is formed. It is yet to be seen if variation of reaction condition or quenching of the reaction mixture at certain point can result in formation of the kinetically more preferable **[d-d]**²⁺ isomer of $[(C_{70})_2]^{2+}$.

Summary and Conclusions

The first spectroscopic characterization of the dimeric fullerene cation complex $[(C_{70})_2]^{2+}(\text{Ti}_3\text{Cl}_{13})^-_2$ is reported and supported by DFT calculations. IR spectrum of the dimer is interpreted in terms of the normal modes of the pristine C_{70} , and the effects of charging C_{70} and the inter-cage bond formation between C_{70} units on the IR spectrum are discussed. NIR absorption and fluorescence spectra of the complex are studied, and the dimer is shown to have a small HOMO-LUMO gap of 0.8 eV. Electronic structure of $[(C_{70})_2]^{2+}$ is studied with the use of DFT and compared to that of the other single-bonded fullerene dimers, including $[(C_{70})_2]^{2-}$, $(C_{69}N)_2$, and $[(C_{60})_2]^{2-}$. Characteristic features in the vibrational spectra and electronic structure of all single-bonded fullerene dimers are revealed

The spectra, electronic structure and energetics of the single-bonded cationic dimer of C_{70} , $[(C_{70})_2]^{2+}$, have been thoroughly studied experimentally and with the use of DFT calculations. IR spectrum of the cationic dimer is reported for the first time and its interpretation in terms of the parent C_{70} fundamentals is fulfilled. It is shown that charging of C_{70} weakly affects its vibrational frequencies and eigenvectors, and so does the dimerization of the cation. Projection analysis revealed that majority of strong IR-active modes of C_{70} appears in the IR spectrum of the dimer with medium to strong intensity. At the same time, analysis of the IR spectra of all single-bonded dimers revealed a characteristic vibration of these

species. In particular, in the IR spectra all single-bonded dimers exhibit a strong absorption in 800-900 range due to the specific vibration of the inter-cage bond.

In the electronic structure all single-bonded dimers are shown to have two specific orbitals, one of which is bonding while another one is antibonding for the inter-cage bond. These levels are lowest unoccupied in the cationic dimer or highest occupied in the anionic dimers as well as in the azafullerene dimers. In the energy scale these levels are located approximately in the middle of the HOMO-LUMO gaps of corresponding fullerenes, resulting in the small gaps of the single-bonded dimers and appearance of the NIR bands in the absorption spectra of the cationic and anionic dimers.

The study of the energetics of the possible isomers of single-bonded dimers of C_{70} revealed that experimentally observed structures of $[(C_{70})_2]^{2+}$ and $[(C_{70})_2]^{2-}$ are the most stable isomers. For the anionic dimer, formation of the experimentally observed isomer is favored by both spin density distribution and local curvature of the carbon atoms (quantified in terms of POAV angles) in C_{70}^- . As a result, experimentally observed isomer of $[(C_{70})_2]^{2-}$ is found to be significantly lower in energy than all other isomers. On the contrary, formation of the experimentally observed isomer of the cationic dimer is favored only by POAV values, while spin density distribution favors different isomers. As a result, experimentally observed isomer of $[(C_{70})_2]^{2+}$ is only slightly more stable than two other isomer, and their isolation can be expected in future.

Acknowledgments. We thank Dr. Robert Bolskar for discussion of the absorption spectra of C_{70}^+ , Dr. Karine Schulte for the discussion of Coulomb interaction in $(C_{59}N)_2$ and Mr. Frank Ziegs for assistance in Raman measurements. Financial support from Alexander von Humboldt Foundation (to A.A.P.) and computer time at the Research Computing Center of MSU are gratefully acknowledged.

Supporting Information Available: DFT-optimized Cartesian coordinates of the dimer molecules, full list of DFT-computed vibrational frequencies and absorption intensities of $[(C_{70})_2]^{2+}$ and $Ti_3Cl_{13}^-$, full list of DFT-computed and experimental C_{70} fundamental frequencies, TD-DFT-computed lowest energy excitations in C_{70}^+ and C_{70}^- , relative energies of the isomers of $[(C_{70})_2]^{2+}$.

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