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Comparative Raman study of the Ti complex $Cp_2\mathrm{Ti}(\eta^2\text{-}\mathrm{C}_{60})\cdot\mathrm{C_6H_5CH_3}$ and $\mathrm{Ti}_x\mathrm{C}_{60}$ films

© A.V. Talyzin, U. Jansson, A.V. Usatov*, V.V. Burlakov*, V.B. Shur*, Y.N. Novikov*

Department of Inorganic Chemistry, Ångström Laboratory,
SE-751 21 Uppsala, Sweden
* A.N. Nesmeyanov Institute of Organoelement Compounds, Russain Academy of Sciences,
117813 Moscow, Russia

Raman spectra from the first Ti fullerene complex $Cp_2\mathrm{Ti}(\eta^2\text{-}\mathrm{C}_{60})\cdot\mathrm{C_6H_5CH_3}$ are presented. Compared to spectra of pure C_{60}, the spectra of the Ti complex exhibit a number of new peaks due to the symmetry lowering for C_{60}. The $A_g(2)$ mode is downshifted by $12\,\mathrm{cm}^{-1}$ compared to C_{60}, which corresponds to charge transfer of one electron per Ti$-$$\mathrm{C}_{60}$ bond. This value ($6\,\mathrm{cm}^{-1}$ for one transferred electron) is identical to the downshift of the $A_g(2)$ mode in alkali metal fullerides with ionic bonding. The spectra of $Cp_2\mathrm{Ti}(\eta^2\text{-}\mathrm{C}_{60})\cdot\mathrm{C_6H_5CH_3}$ were compared to the spectra of evaporated $\mathrm{Ti}_x\mathrm{C}_{60}$ films. The $A_g(2)$ mode in $\mathrm{Ti_4C_{60}}$ showed a downshift of about $25\,\mathrm{cm}^{-1}$ compared to pure C_{60}, which corresponds to charge transfer of one electron per Ti atom, similar to the ionic alkali metal fullerides and different from a η^2-C_{60} type of bonding.

The Raman spectroscopy is widely used for characterization of different C_{60} compounds. The effect of different kinds of bonding on the Raman spectra is now established for many C_{60}-based materials; stronger bonding gives new peaks, some of the silent modes can appear, and a number of C_{60} modes became split due to lowering of molecular symmetry [1–4]. In many cases the shift of the $A_g(2)$ mode is very sensitive to the structural modifications of the C_{60}. For example, softening of the A_g (2) mode was widely used for characterization of stoichionetry in $\mathrm{M}_x\mathrm{C}_{60}$ alkali metal fullerides since it had been found that the dowshift is linearly dependent on the number of intercalating metal atoms with a typical value of downshift $\sim 6\,\mathrm{cm}^{-1}$ per transferred electron [1]. Other compounds with strong covalent bonding also exhibit similar downshift of $5-6\,\mathrm{cm}^{-1}$ [2–4]. In contrast, weaker donor-acceptor bonding with partial charge transfer from ligand to C_{60} leads to a much smaller downshift and for van der Waals bonding the position of $A_g(2)$ mode of C_{60} remains unchanged [5,6].

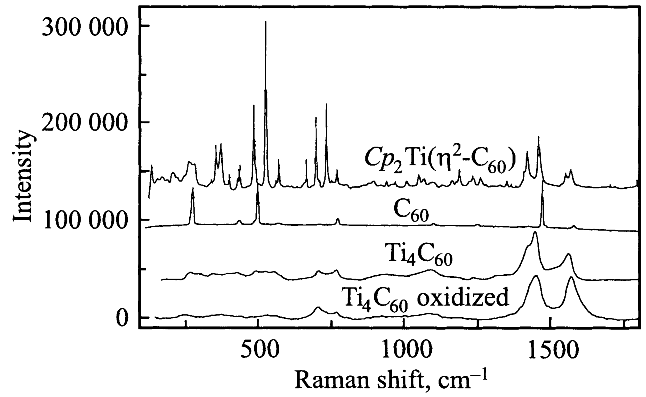
Valuable information can be obtained using Raman spectroscopy for new amorphous materials, such as $\mathrm{Ti}_x\mathrm{C}_{60}$ which recently was deposited as a thin films by co-evaporation of Ti and C_{60} [7]. The nature of bonding in this compound is still unclear although it was suggested that Ti is covalently bonded to C_{60}. The recent discovery and structural characterization of the first fullerene Ti complex $Cp_2\mathrm{Ti}(\eta^2\text{-}\mathrm{C}_{60})$ gives a possibility to study the effects of covalent Ti$-$$\mathrm{C}_{60}$ bonding on Raman spectra [8]. In the present contribution we report the first Raman study of this complex and compare it with the spectra of $\mathrm{Ti_4C_{60}}$ films.

1. Experimental

The details of the preparation and structural characterization of the $Cp_2\mathrm{Ti}(\eta^2\text{-}\mathrm{C}_{60})\cdot\mathrm{C_6H_5CH_3}$ were reported elsewhere [6]. In this compound, toluene molecules form weak van der Waals bonds similar to known solvates of pure C_{60}. Thin films of $\mathrm{Ti}_x\mathrm{C}_{60}$ were deposited by co-evaporation of C_{60} and Ti under UHV conditions. Details of the experimental setup were published elsewhere [5]. A film with composition $\mathrm{Ti_4C_{60}}$, as determined by XPS, was deposited on the glass substrate and capped with Ti to prevent the sample against oxidation. Raman spectra of $\mathrm{Ti_4C_{60}}$ were recorded through the glass substrate using Renishaw Raman 2000 spectrometer with 514 nm excitation wavelengths and resolution of $2\,\mathrm{cm}^{-1}$. If the Ti capping layer had microholes, it was possible to observe with optical microscope how the colour of the film is changed due to oxidation around such holes. The process was sufficiently slow to record the spectra from the same spot before and after oxidation. Raman spectra of the $Cp_2\mathrm{Ti}(\eta^2\text{-}\mathrm{C}_{60})\cdot\mathrm{C_6H_5CH_3}$ were recordered in the sealed ampoule filled with argon through the glass using 785 nm laser.

2. Results and Discussion

2.1. Ramam spectrum of the $Cp_2\mathrm{Ti}(\eta^2\text{-}\mathrm{C}_{60})\cdot\mathrm{C_6H_5CH_3}$. Let us first analyse the Raman spectrum of the $Cp_2\mathrm{Ti}(\eta^2\text{-}\mathrm{C}_{60})\cdot\mathrm{C_6H_5CH_3}$. As can be seen in Figure, this spectrum exhibits a number of new peaks compared to pure C_{60}. Raman spectra of C_{60} solvates are almost identical to pure C_{60}, and the presence of toluene in the structure should not affect Raman modes of C_{60} significantly [6]. Lines of toluene are very weak, and only the strongest line at $1008\,\mathrm{cm}^{-1}$ can be identified in our spectra. The other lines are a combination of C_{60}-derived modes and vibrations of the Cp_2Ti-group. Some of the vibrational modes of the Cp_2Ti-group can be identified by comparison with the Raman spectrum of $Cp_2\mathrm{TiCl_2}$. The assignment of the vibrational modes for $Cp_2\mathrm{TiCl_2}$ was made according to the data by Holubova et al. [9]. From the similarity of the compounds we can expect some of the modes in the $Cp_2\mathrm{TiCl_2}$ spectrum to be similar to those of Ti$-$$\mathrm{C}_{60}$ complex. Indeed, C$-$H modes of $Cp_2\mathrm{TiCl_2}$ situated at 843, 864 and $1074\,\mathrm{cm}^{-1}$ can be identified with weak



Raman spectrum of the Cp_2Ti(η^2-C$_{60}$) compared to the spectra of pure C$_{60}$, Ti$_4$C$_{60}$ and oxidized Ti$_4$C$_{60}$.

peaks at 881, 894 and 1095 cm^{-1}. Peak of Cp vibrations at 394 cm^{-1} for Cp_2TiCl$_2$ probably can be identified with a peak at 400 cm^{-1} for Ti–C$_{60}$ complex. Peaks of Ti–Cp vibrations of niobocene dichloride are at 412, 301 cm^{-1} and corresponding peaks in the Cp_2Ti(η^2-C$_{60}$) are most probaly located first at 430 cm^{-1} and second at 280 or 337 cm^{-1}. It is very interesting that Cp_2Ti(η^2-C$_{60}$) spectra exhibit a sharp peak at 134 cm^{-1} which probably can be associated with vibrations due to Ti bonded to C$_{60}$. C–C vibrations of titanocene dichloride are more difficult to identify with Cp_2Ti(η^2-C$_{60}$) because in the same spectral region there are several peaks, some of them from C$_{60}$ vibrations.

All other peaks in the spectra of Cp_2Ti(η^2-C$_{60}$) originate from C$_{60}$. The $A_g(2)$ mode is downshifted compared to pure C$_{60}$ by 12 cm^{-1}. Taking into account that Ti forms two bonds with two carbon atoms from C$_{60}$ molecule, we calculated a shift of 6 cm^{-1} per bond. This is very similar to the alkali metal fullerides which exhibit a downshift of the $A_g(2)$ mode by 6 cm^{-1} per transferred electron. The $H_g(7)$ and $H_g(8)$ modes of C$_{60}$ are split in the Cp_2Ti(η^2-C$_{60}$) and can be found at 1407, 1417 cm^{-1} and 1546, 1563 cm^{-1}. $H_g(5)$ and $H_g(6)$ modes are also split into several weak peaks. Four strong peaks and several weak peaks can be found also around 600–800 cm^{-1} which are typically ascribed to $H_g(3)$ and $H_g(4)$ derived for different kinds of C$_{60}$ complexes and polymers. The strongest peaks in the spectrum of the Cp_2Ti(η^2-C$_{60}$) are ones at 484 and 526 cm^{-1}. The first peak can be assigned to the downshifted $A_g(1)$ mode and the second peak, to typcally silent infrared-active mode $F_{1u}(1)$ of C$_{60}$. The $H_g(1)$ mode is split into several components which are represented as weak peaks around 240–290 cm^{-1}. $H_g(2)$ mode is split into two sharp peaks at 430 and 436 cm^{-1}. Some other weak peaks can be also assigned to different silent and infrared-active modes. The main conclusions which can be drawn from the above discussion is that lowering of the C$_{60}$ symmetry lead to splittings and shifts of most modes, activation of silent and infrared modes. The shift of the $A_g(2)$ mode allows us to draw the conclusion that η^2 bonding between Ti and C$_{60}$ leads to charge transfer of two electrons, one electron per Ti–C bond.

2.2. Ramam spectra of the Ti$_4$C$_{60}$ films. The spectra of the unoxidized Ti$_4$C$_{60}$ is clearly different from those of pure C$_{60}$. The main signature of the chemical bonding in this material is a shift of the $A_g(2)$ mode to 1443 cm^{-1} which is 26 cm^{-1} lower then in pure C$_{60}$. Other modes of the C$_{60}$ are also shifted or splitted. $H_g(7)$ and $H_g(8)$ modes can be found at 1416 and 1554 cm^{-1}, which corresponds to a downshift compared to pure C$_{60}$ by 10 and 22 cm^{-1}, respectively. The $H_g(1)$ mode is clearly split into three components at 257, 265 and 293 cm^{-1}. A group of new peaks is observed at 330–400 cm^{-1}. The peak at 425 cm^{-1} can be assigned to the $H_g(1)$ mode while the peak at 490 cm^{-1}, to $A_g(1)$ mode. The peaks at the 522 and 553 cm^{-1} belong, most likely, to the activated infrared modes $F_{1u}(1)$ and $F_{1u}(2)$. Peaks at 707 and 766 cm^{-1} can be assigned to $H_g(3)$ and $H_g(4)$ modes, respectively. Very typical features of Ti$_4$C$_{60}$ are two broad peaks around 939 and 1089 cm^{-1}. The nature of these peaks is unknown but it can be clearly seen that they strongly decrease their intensity after oxidation. It is known that Ti$_x$C$_{60}$ is extremely sensitive towards oxidation. This observation is confirmed by the comparison of the Ti$_4$C$_{60}$ Raman spectra with the spectrum of the same film after oxidation, measured through a microhole in the capping layer. The oxidation can be observed as a change in color using optical microscope. Other remarkable changes due to oxidation are strong decrease of the $A_g(2)$ intensity with simultaneous upshift by 6 cm^{-1}, upshift of the $H_g(7)$ and $H_g(8)$ modes by 12 and 10 cm^{-1}, respectively, and a strong change of relative intensity for other peaks, e.g., peaks at 707 and 766 cm^{-1}. It shall be noted that spectra of oxidized Ti$_4$C$_{60}$ shown in Figure was recordered within one hour of exposure to the air. Longer exposure leads to complete degradation of the sample. It is interesting to note that peaks in the spectra of the Ti$_4$C$_{60}$ are much broader compared to those in the spectrum of the Ti complex. Most probably it can be explained by stronger disorder in the amorphous Ti$_4$C$_{60}$.

Several different structural models can be proposed for Ti$_x$C$_{60}$. Donor-acceptor η^6-C$_{60}$ bonding have been theoretically studied by Saito et al. [10]. This kind of bonding suggested a charge transfer of 0.25 electrons from Ti to C$_{60}$, which would result in much smaller shift of the $A_g(2)$ mode compared to observed value of 6 cm^{-1} per metal atom. Therefore this possibility must be ruled out for our samples. Ionic bonding similar to alkali metal fullerides and covalent bonding have been discussed by Norin et al. [7]. Different structural models can be proposed for covalent bonding of Ti and C$_{60}$. A probable model is η^2-C$_{60}$ bonding when Ti has two bonds with neighbouring carbon atoms of the C$_{60}$. Other kind of bonding was reported for Pd$_x$C$_{60}$ where Pd served as a bridge between two neighbouring C$_{60}$ molecules. Similar polymeric structure can also be suggested for Ti$_x$C$_{60}$. Using the Raman spectra of the Cp_2Ti(η^2-C$_{60}$) we can rule out η^2-C$_{60}$ bonding for Ti$_x$C$_{60}$, because it is clear that each Ti–C_{60} bond results in charge transfer of one electron in the $Cp_2\mathrm{Ti}(\eta^2\text{-}C_{60})$. Since each Ti atom forms two bonds with C_{60} in $Cp_2\mathrm{Ti}(\eta^2\text{-}C_{60})$, the resulting shift value is 12 cm^{-1} per metal atom, which is different from 6 cm^{-1} per Ti atom observed for Ti_4C_{60}. It is therefore possible to suggest that Ti form an intercalation compound similar to alkali metal fullerides or that Ti is bonded to C_{60} with single bonds, e. g., in dimers with Ti serving as a bridge.

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