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Manifestations of noncovalent interactions between chloroform and dimethyl sulfoxide in vibrational absorption and Raman spectra

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Vibrational spectroscopy (IR absorption and Raman scattering) revealed the formation of complexes with a hydrogen bond between chloroform and dimethyl sulfoxide in carbon tetrachloride. Experimental observations were interpreted in the framework of ab initio calculations performed using the GAUSSIAN 16 package.

Keywords: vibrational Raman and IR absorption spectra, solution in CCl_4, chloroform, dimethyl sulfoxide, hydrogen bond, ab initio calculations.

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Introduction

Chloroform (Cl_3CH) is a typical representative of CH donors. When interacting with electron-donor molecular systems, they form complexes with weak hydrogen bonding, which in some cases exhibits unusual spectroscopic and geometric properties [1–3]. This molecule belongs to the group of compounds with pronounced anesthetic properties necessary for the successful implementation of invasive surgical procedures. One of the currently considered physicochemical reasons for the appearance of an anesthetic effect is the ability to block excitation signals due to the formation of a weak hydrogen bond with target sites with increased electron density (lone pairs, π-electronic systems, etc.). A common method for detecting this type of nonvalent interactions is infrared (IR) absorption spectroscopy, where the effect of hydrogen bond formation is identified by a shift and a change in the integral intensity of the band of stretching vibration A–H [4–7]. The formation of complexes with hydrogen bonding between chloroform (Cl_3CH) and such a strong electron donor as dimethyl sulfoxide ($(CD_3)_2SO$) was detected in this study by changes in the spectra of both IR absorption and Raman scattering in solutions in carbon tetrachloride (CCl_4). As far as we know, as an electron-donating compound $(CD_3)_2SO$ was used only in the study of complexes with a relatively strong hydrogen bond, as well as dimerization and self-association of dimethyl sulfoxide in the liquid phase and in mixtures with water [8–10]. The spectroscopic measurement data is in reasonable agreement with the results of quantum chemical calculations.

Experimental and calculation procedure

Measurements at room temperature in CCl_4 solution, first using IR absorption spectra, were carried out in the range of wavenumbers $4000-700\,cm^{-1}$ with a resolution of $2\,cm^{-1}$ in areas free from strong solvent absorption. An IR Fourier spectrometer (Nicolet 6700) with a KBr beam splitter and a DTGS detector was used. The spectra of the solutions were recorded with 64 scans using a cuvette with an optical length of 0.63 mm and NaCl windows. The main attention was paid to the region of stretching vibrations of the CH group of chloroform, as well as the $1000-1100\,cm^{-1}$ regions, where a number of bands with vibrations of the SO and CD_3 groups of deuterosubstituted dimethyl sulfoxide are located. The use of the deuterosubstituted form $(CD_3)_2$) is associated with the need to eliminate the overlap of the bands of the CH groups of the donor and acceptor. The concentrations of the solution components were in the range of 0.05–1 mol/l.

Then the Raman spectra were recorded on a Horiba Yobin-jvon LabRam HR800 instrument. A solid-state laser with a power of 100 MW and a wavelength of 532 nm was used as the excitation source. The spectrometer is fitted with an Olympus BX41 microscope with a lens 10×. The radiation power incident on the sample was 15 mW. The scattered radiation (without separation of parallel and perpendicular polarization components) was analyzed with an 1800 lines/mm grating spectrometer. The spectral resolution ranged from 2 to $3\,cm^{-1}$ in the measurement range from 100 to $3500\,cm^{-1}$. The instrument was calibrated according to a standard made of silicon ($520.7\,cm^{-1}$). The signal was recorded by a detector cooled to $-70°C$. Satisfactory separation of the signal from the noise was achieved with 100 repetitions of recording each point of the recorded spectrum. The instrument is provided with the LabSpec program for recording and processing the spectrum. A glass cuvette and mixtures with significantly higher concentrations, in the range of 0.5–2, mol/l, were used for recording the Raman spectra. The final analysis and processing of both IR absorption and Raman spectra was carried out using the Origin software package.

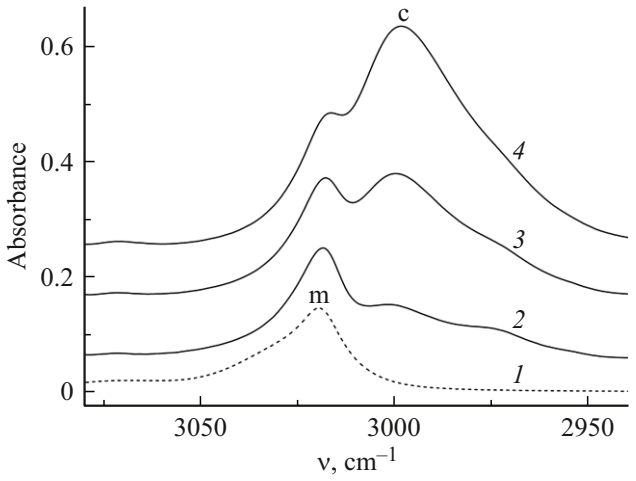


Figure 1. Changes in the IR absorption spectrum of a solution of chloroform and dimethyl sulfoxide in CCl_4 in the region of the CH stretching vibration band band of chloroform with an increase in the concentration of c dimethyl sulfoxide (m — spectrum of the monomer Cl_3CH, c — complex spectra): $c(Cl_3CH) \sim 0.2$ mol/l (*1*–*4*); c(DMSO$\sim$ 0.1 (*2*), 0.2 (*3*), 0.6 mol/l (*4*).

The calculations were performed using the GAUSSIAN 16 Rev. A.03 software package [11]. The calculations were performed using both DFT methods with the wB97XD and B3LYP functionals with the gd3 option, as well as in the framework of perturbation theory of the second (MP2) and fourth orders (MP4sdq) [12–15]. The basic set was selected based on the availability of computer resources and reproducibility of the detected spectroscopic effects. The geometry, interaction energy, and frequencies of normal vibrations of the complex were obtained taking into account the superposition error of the basis (BSSE) [16,17].

Measurement results

Fig. 1 is an example of the observed changes in the IR absorption spectrum of a mixture of $Cl_3CH + (CD_3)_2SO$ in CCl_4 in the region of the stretching vibration of the CH group of chloroform with an increase in the concentration of one of the partners (in this case — $(CD_3)_2SO$). On the low-frequency side of the CH stretching vibration band of the chloroform monomer, a band is recorded, the intensity of which increases strongly with increasing concentration $(CD_3)_2SO$. Its significant broadening is noted, the full width at half maximum (FWHM) is $\sim 50\,cm^{-1}$ (monomer $\sim 10\,cm^{-1}$). The low-frequency shift, broadening, and increase in the intensity of this band correspond to signs of the formation of a complex with a hydrogen bond CH...OS. The fact of complex formation is also recorded along an intense band in the $\sim 1070\,cm^{-1}$ region, free from the interfering influence of solvent bands (Fig. 2). This band is usually attributed to the stretching vibrations of the SO [18,19] bond, as can be seen, it experiences a low-frequency shift close to $6\,cm^{-1}$. The analysis of changes in absorption bands in the region of stretching vibrations of CD_3 dimethyl sulfoxide was not carried out due to the interfering effect of the combination bands.

The measurement results from the Raman spectra are shown in Fig. 3 . the region of CH stretching vibrations of chloroform, Fig. 4 —the region $1000-1900\,cm^{-1}$ of stretching vibration SO and bending vibrations CD_3 of dimethyl sulfoxide, Fig. 5 — the region of CD_3 stretching vibrations $(CD_3)_2SO$ (the change in the most intense band is analyzed). The result obtained for the region of the vibration of CH group of chloroform practically does not differ from

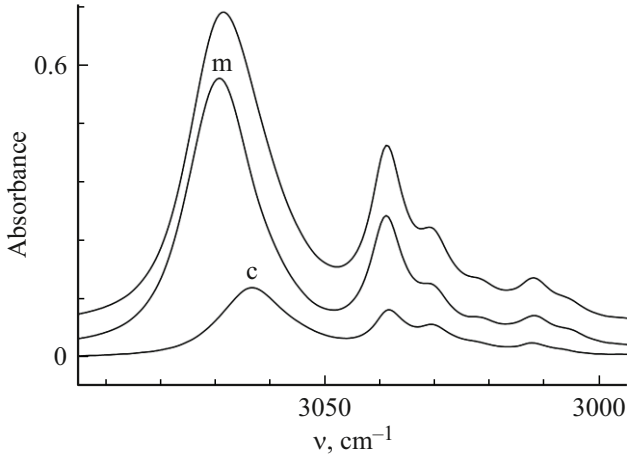


Figure 2. The effect of complex formation in the IR absorption band for the stretching vibration of SO, $c(Cl_3CH)\sim 0.2$ mol/l, c(DMSO) ~ 0.08 mol/l: $\Delta\nu^{c\text{-}m} \sim -6\,cm^{-1}$, upper curve — mixture spectrum, middle — monomer spectrum, lower — the spectrum of the complex as a result of subtraction from the spectrum of a mixture of monomer spectra. For convenience, the spectra are shifted vertically.

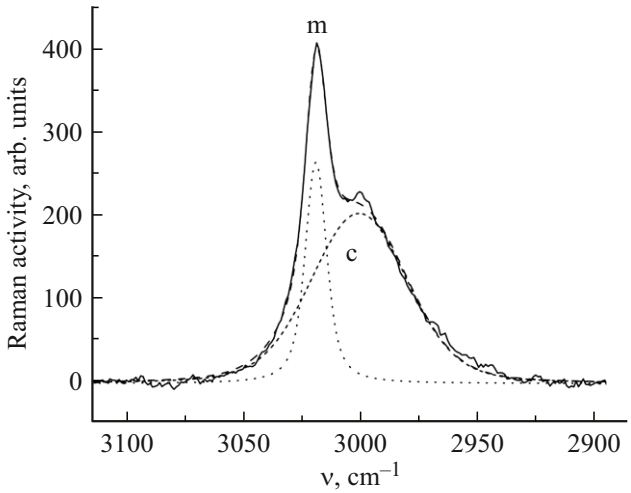


Figure 3. The effect of complex formation on the Raman band for the stretching vibration CH of chloroform (m — monomer spectrum Cl_3CH, c — complex spectra), $c(Cl_3CH) \sim 0.9$ mol/l, c(DMSO$\sim$ 1.7 mol/l: $\Delta\nu^{c\text{-}m} \sim -21\,cm^{-1}$, solid curve — spectrum of the mixture, dotted curve — spectrum of the monomer, dashed curve — spectrum of the complex.

Table 1. Measured spectroscopic parameters of individual bands of Cl_3CH, $(CD_3)_2SO$ and their mixtures in solution in CCl_4 at room temperature

Assignment	IR		Raman spectra		References
	Cl_3CH				
	ν, cm^{-1}		ν, cm^{-1}		
Q(CH)	3020		3020		3016^{liq} [20]
Q(CCl)			671.5		671.1^{gas} [20]
	$(CD_3)_2SO$				
	ν, cm^{-1}		ν, cm^{-1}		
$Q_s(CD_3)$	—		2128		2125_{liq} [18]
Q(SO)	1069		—		1069_{inCCl_4} [18]
$\delta_s(CD_3)$	—		1012		1010_{liq} [18]
complex					
	ν, cm^{-1}	$\Delta\nu^{c\text{-}m}$, cm^{-1}	ν, cm^{-1}	$\Delta\nu^{c\text{-}m}$, cm^{-1}	
$Q(CH)^{compl}$	2999	−21	2999	−21	
$Q_s(CD_3)^{compl}$	–	–	2129	+1	
$Q(SO)^{compl}$	1063	−6			
$\delta_s(CD_3)^{compl}$			1013	+1	
$Q(CCl)^{compl}$			666.5	−5	

that obtained by the IR absorption method in terms of band shift and broadening. However, unlike IR absorption, there is no significant increase in the intensity of raman for this band in the complex. A qualitativelydifferent picture is observed in the region of 1000−1100 cm^{-1} (Figs. 4 and 2). In the Raman spectrum, the band at 1012 cm^{-1} is intense, experiencing only a small high-frequency shift of $\sim +1$ cm^{-1} during complex formation (isolation of this band is hampered by the presence of a solvent band on the low-frequency side (CCl_4)). The strong band detected in the IR absorption at $\sim$ 1070 cm^{-1} is practically absent in the Raman spectrum. The results of individual spectroscopic measurements are collected in Table 1. The interpretation for the chloroform bands is tied to the data known from the literature [20].

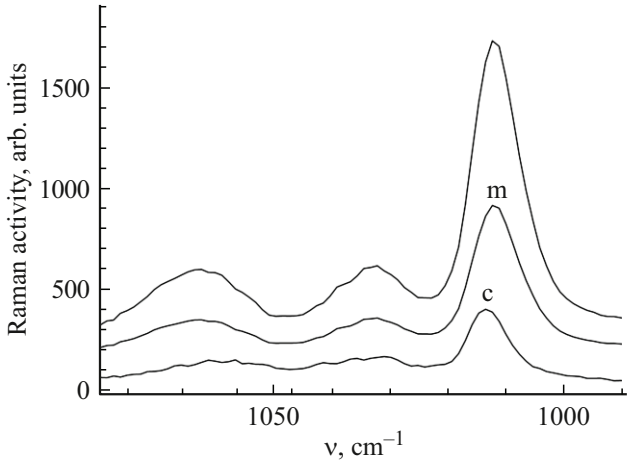


Figure 4. The effect of complex formation on the Raman band for bending vibrations of CD_3. $c(Cl_3CH) \sim 0.9$ mol/l, $c(DMSO) \sim 0.9$ mol/l: $\Delta\nu^{c\text{-}m} \sim +1$ cm^{-1}, upper curve —mixture spectrum, middle — monomer spectrum, lower — spectrum complex as a result of subtraction from the mixture spectrum of monomer spectra, for convenience the stripes are shifted vertically.

Calculation results and discussion

The calculations were performed using the GAUSSIAN-16 software package. Using the second-order perturbation theory (MP2), a qualitatively correct description of spectroscopic changes in the region of chloroform bands can be obtained already with relatively weak bases, starting from 6-31++G(d,p). However, an adequate comparison with the results of this experiment in the 1000−1100 and cm^{-1} regions, where the vibration bands of the SO and CD_3 dimethylsulfoxide groups are located, becomes possible only when switching to the extended 6-311++G(3df,3pd) basis. It should be noted that overestimated values of the wave numbers of normal vibrations are typical for calculations in

Table 2. Spectroscopic parameters of Cl_3CH, (CD3)2SO monomers and the $Cl_3CH{\cdot}(CD_3)_2SO$) complex, calculated at the MP2/6-311++G(3df,3pd) level

N	Assignment	Complex			Monomers				$\Delta\nu^{c\text{-}m}$ cm^{-1}
		ν, cm^{-1}	I, km/mol	R_a, Å^4/amu	ν, cm^{-1}	type	I, km/mol	R_a Å^4/amu	
1	Q(CH)	3167	188	143	3215	A_1	1.7	62	−48
2	q_s(CD)	2371	0.19	42	2371	A′	0.26	42.6	0
3	q_a(CD)	2368	0.014	12.5	2368	A′	0.09	16.7	0
4	q_s(CD)	2364	0.21	37.9	2364	A′	1.8	43.8	0
5	q_a(CD)	2362	0.072	6.5	2362	A″	0.003	4.4	0
6	q_a(CD)	2198	1.8	136	2197	A′	1.6	145	1
7	q_a(CD)	2197	0.28	16.4	2197	A″	0.44	0.03	0
8	δ(CH)	1321	22.8	1.2	1273	E	40	4.2	48
9		1316	19.7	4.9					43
10	Q(SO)	1119	154	9.8	1140	A′	151	10.6	−21
11	δ_s(CD)	1076	33	1.2	1079	A′	21.2	0.96	−3
12	δ_aCD)	1064	1.1	3.3	1066	A″	0.2	3.5	−2
13	δ_s(CD)	1063	0.79	2.7	1063	A′	0.69	4.0	0
14	δ_s(CD)	1054	4.1	9.6	1052	A′	7.4	13.6	2
15	δ_a(CD)	1052	3.8	4.4	1052	A″	5.1	0.24	0
16	δ_a(CD)	1048	7.3	2.6	1045	A″	6.7	4.2	3
17	δ(SCD)	842	16.6	0.89	838	A′	14.2	0.62	4
18	Q(C-Cl)	814	139	4.6	813	E	264	7.2	1
19		796	122	3.2					−17
20	δ(SCD)	787	1.3	1.2	784	A′	0.79	1.1	3
21	Q_a(CS)	779	10.6	1.8	775	A″	16	2.3	4
22	Q(C−Cl), δ_s(C-Cl_3)	692	12.9	13.3	700	A_1	3	11.8	8
23	δ(SCD)	689	0.29	0.44	685	A″	0.55	0.45	4
24	Q(CS)	639	1.7	15.3	635	A′	3.7	20.9	4
25	δ(SCD)	636	2.5	5.8	629	A″	4.3	7.5	7
26	δ(ClCCl)	383	2.8	5.6	382	A_1	0.16	5.9	1
27	δ(OCS)	338	7.5	1.2	335	A′	6.6	1.2	3
28	δ(CO)	300	8.0	2.4	298	A″	8.4	2.9	2
29	δ(ClCCl)	273	0.31	1.9	272	E	0.06	4.4	1
30		272	0.03	1.9					0
31	δ(CSC)	254	0.62	1.5	255	A′	0.26	2.1	1
32	τ_s(CD_3)	190	1.3	0.18	186	A′	0.51	0.09	4
33	τ_a(CD3)	149	0.21	0.016	141	A″	0.007	0.04	8
34	τ(O-S-C)	109	11.6	0.51	–	–	–	–	–
35	σ(S-C)	56	3.9	0.23	–	–	–	–	–
36	τ(Cl-C-S)	50	0.32	0.90	–	–	–	–	–
37	τ(C-S-C-Cl)	42	1.04	0.61	–	–	–	–	–
38	τ(C-S-C-Cl)	34	0.20	0.39	–	–	–	–	–
39	τ(S-C)	23	1.99	0.15	–	–	–	–	–

the harmonic approximation. The optimized geometry for the most stable dimer structure (absence of imaginary/negative frequencies) is shown in Fig. 6. As can be seen, the dimer is characterized by a nonlinear structure that is stabilized by the main hydrogen bond O...H (R(O...H) = 2.0289 Å) and two additional van der

Table 3. Change in the wavenumber of the (C-H) stretching vibration band of chloroform during complex formation with DMSO, depending on the calculation method based on 6-31++g(2d.2p)

Method	wB97XD	B3LYP, gd3	B3LYP$^{anh.}$, gd3	MP2	MP4sdq	Exp
ω^{m}, cm^{-1} (I), km/mol	3212.5 (1.6)	3171.6 (1.5)	3031.1 (0.32)	3219.4 (1.5)	3214.0 (0.58)	3020 –
ω^{c}, cm^{-1} (I), km/mol	3102.1 (275)	3071.6 (300)	2925.6 (275)	3146.1 (247)	3180.8 (193)	2999 –
$\Delta\omega^{c\text{-}m}$, cm^{-1}	−110.4	−100	−105.5	−73.3	−33.2	−21

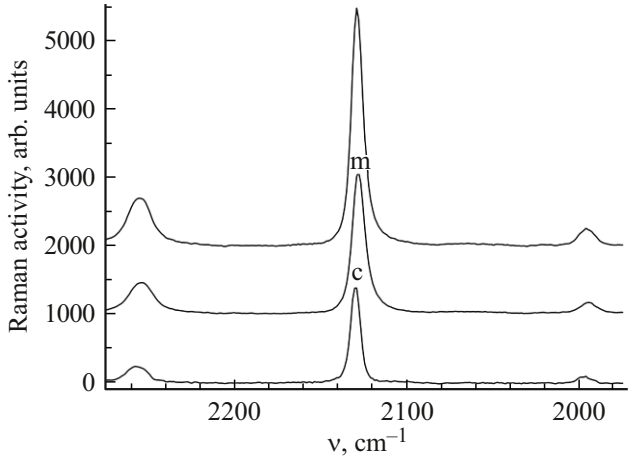


Figure 5. The effect of complex formation on the Raman band for stretching vibrations CD_3, $c(Cl_3CH) \sim 0.9$ mol/l, c(DMSO~ 0.9 mol/l: $\Delta\nu^{c\text{-}m} \sim +1\,cm^{-1}$, upper curve —mixture spectrum, middle — monomer spectrum, lower — the spectrum of the complex is the result of subtraction from the spectrum of a mixture of monomer spectra, for convenience, the bands are shifted vertically.

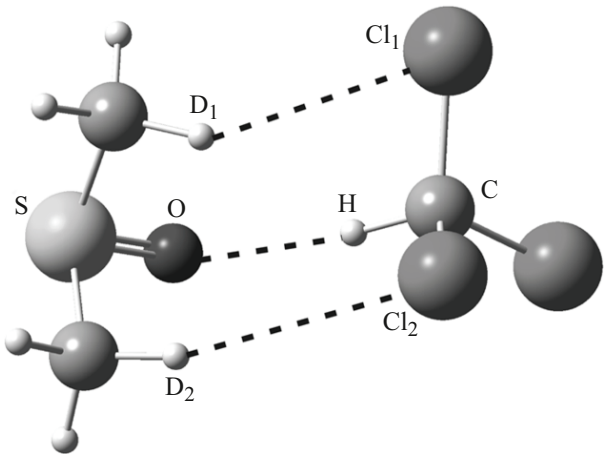


Figure 6. The geometry of the complex is calculated at the MP2/6-311++G(3df,3pd) level. $R(O...H) = 2.0289$ Å, $R(D1...Cl1) = 3.248$ Å, $R(D_2{\cdot}Cl_2) = 3.09047$ Å, $\angle(SOH) = 130.27658°$, $\angle(CHO) = 161.15907°$, Dih(SOHC) = 9.44376°.

Waals contacts such as D...Cl ($R(D1...Cl1) = 3.248$ Å, $R(D2...Cl2) = 3.0905$ Å).

The wave numbers of normal vibrations in the harmonic approximation are given in Table 2. The assignment of vibrations to the type of motion of monomer atoms and the complex was carried out based on the analysis of data from the GausView application and comparison with the results from literature [18–20]. The calculated value of the enthalpy of dimer formation is 7.5 kcal/mol (taking into account zero fluctuations of 7 kcal/mol), which corresponds to the upper limit of the weak hydrogen bond. It should be noted that the calculated value of the raman scattering activity for the band at 1012 cm^{-1} appears to be underestimated. The result can be improved on the assumption that three bands slightly different in position with a predominant contribution from the bending vibrations of the CD_3 groups are recorded as a single band (FWHM$\sim 12-14\,cm^{-1}$).

The observed shifts of the bands of the complex in the region of stretching vibrations of the CH chloroform and SO dimethyl sulfoxide groups are reproduced by calculations only at a qualitative level. They are noticeably weaker than the predicted low-frequency band shift. The reasons can be found in the presence of anharmonic effects, as well as in the choice of the calculation method. Table 3 presents the results of calculating the shift of the chloroform CH band with an improvement in the calculation method from DFT with functionals with empirical variance to fourth-order perturbation theory, obtained with the same basic set. It can be seen that the shift decreases noticeably with the improvement of the calculation method. An assessment of the influence of anharmonicity has shown that, unlike strong complexes [21–24] taking into account the anharmonicity of the resonant type here does not lead to a significant shift change. In fact, its absolute value slightly increases.

Conclusion

It follows from the nature of changes in the RS and IR absorption spectra in the CCl_4 solution, that chloroform, when interacting with dimethyl sulfoxide, forms complexes with a hydrogen bond characterized by a noticeable low-frequency shift, a strong increase in absolute intensity, and a multiple ($\sim$ fivefold) broadening of the band of stretching

vibration of the CH group. A very slight high-frequency shift of the bands of stretching vibrations of the CD_3 group, characteristic of the vicinal bonds of the proton acceptor, was recorded in the Raman spectrum [24]. Two bands are distinguished in the $1000-1100\,cm^{-1}$ regions: one in the IR absorption ($\sim 1070\,cm^{-1}$) with a low-frequency shift during complex formation and the second in the RS ($\sim 1012\,cm^{-1}$) with a slight high-frequency shift. The first is attributed to the stretching vibration of the SO group, and the second —to the bending vibrations of the CD_3 group. For bands with a large scattering cross-section, the Raman spectrum agrees with the results of IR absorption and complements them in areas with interfering solvent absorption.

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Conflict of interest

The authors declare that they have no conflict of interest.

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