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Phonons and electron-phonon interaction in halogen-fullerene compounds

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We have investigated the optical spectra of different halogen-fullerene compounds: $C_{60}I_{4-x}$, $C_{70}I_2$, $C_{60}Br_{24}$, $C_{60}Cl_{24}$, and $C_{70}Cl_{17}$. Two types of carbon-halogen bonding have been established: (a) $C_{60}I_{4-x}$ and $C_{70}I_2$ compounds are formed by a C_{60} or C_{70} molecule sublattice and an I_2 molecule sublattice that weakly interact via van der Waals forces; (b) $C_{60}Br_{24}$, $C_{60}Cl_{24}$, and $C_{70}Cl_{17}$ compounds are characterized by covalent bonds between C and Br/Cl atoms. We have studied in detail the resonance effects in $C_{60}Cl_{24}$ using the methods of Raman scattering, infrared absorption, and absorption in the visible region. The effect originates from the interactions between the phonon subsystem and the electron band at 2.33 eV and manifests itself in a resonant enhancement of the Raman line intensities and in the repetition of the phonon and the luminescence spectra shifted by the frequency of Raman-active phonon at 1508 cm^{-1}. The group-theory analysis of phonon symmetries in rigid and nonrigid $C_{60}Br_{24}$ and $C_{60}Cl_{24}$ crystals has been performed. [S0163-1829(98)04710-9]

I. INTRODUCTION

Optical studies of fullerenes doped by various atoms and molecules are of a great interest during the last years. Raman spectra of the alkali-doped fullerenes were extensively studied due to superconductivity discovered in $C_{60}M_x$ ($x\approx 3$) compounds whereas few papers were devoted to halogen-fullerene compounds.[1,2] These compounds attracted attention since one could expect to observe there the effects similar to those discovered in nonsuperconducting alkali-doped compounds.[3,4] The most pronounced effects were observed in the Raman spectra of $C_{60}M_6$ ($M=$K, Rb, Cs) compounds. In particular, the tangential modes of solid C_{60} (including the most intense A_g line at 1469 cm^{-1}) were found to soften in the Raman spectra of $C_{60}M_6$ by $\sim 50\ \mathrm{cm}^{-1}$.[3] This effect was attributed to the charge-transfer-induced elongation of the intraball C-C bond lengths. In the case of donor dopants, these distortions lead to the softening of the phonon frequencies. Really, when studying the $C_{60}I_x$ and $C_{70}I_x$ compounds, the softening of the I_2-molecule vibration (being at 213 cm^{-1} in a free molecule[5]) by $\sim 15\ \mathrm{cm}^{-1}$ was found.[2] In addition, in the Raman spectra of $C_{60}I_x$ compounds the author has observed an additional shoulder at 1459 cm^{-1} of the intense A_g line in the xx and yy polarizations. All these effects were interpreted as a result of a donor-acceptor interaction due to a charge transfer between C_{60} (or C_{70}) and I_2 molecules.

In contrast, the brominated fullerenes $C_{60}Br_6$, $C_{60}Br_8$, and $C_{60}Br_{24}$ reveal the Raman spectra completely different from those in C_{60} compounds.[1] In particular, the line corresponding to a vibration of a free Br_2 molecule [317 cm^{-1} (Ref. 5)] was absent in the spectra whereas the lines in the spectral region of C-Br bonds [$\sim 600\ \mathrm{cm}^{-1}$ (Ref. 6)] appeared.

In this paper we present a systematic study of Raman spectra of $C_{60}I_{4-x}$, $C_{70}I_2$, $C_{60}Br_{24}$, $C_{60}Cl_{24}$, and $C_{70}Cl_{17}$ compounds. In Sec. III, we discuss the character of halogen-carbon bonds in these compounds. Our conclusion about the absence of noticeable charge transfer in iodine-doped fullerenes contradicts the results of Ref. 2. Section IV is devoted to a comprehensive study of resonance effects in $C_{60}Cl_{24}$ including Raman scattering, infrared absorption, and absorption in the visible region. The resonance Raman scattering in the parent fullerenes C_{60} and C_{70} and in the alkali-doped $C_{60}M_x$ compounds was observed when studying the dependence of Raman-line intensities on the excitation frequency.[7–9] However, there were no experimental evidences on resonance effects in halogen-fullerene compounds.[1,2]

The interpretation of spectra is supported by a group-theory analysis presented in the Appendix. The phonon symmetry analysis was performed both in rigid and nonrigid crystal models. The introduction of nonrigid crystal with rotating halogen-fullerene molecules allows to predict a fine structure of the vibrational spectra as was made previously for the nonrigid parent C_{60} crystal.[10]

II. EXPERIMENTS

Fullerene containing soot was prepared by evaporation of graphite in a dc arc at the current 100 A in a helium atmosphere of 180 torr pressure. Fullerenes were Soxhlet extracted from soot with toluene. Then C_{60} and C_{70} were isolated from the fullerene mixture by column chromatography on graphite powder as a stationary phase with particle sizes ranging from 80 to 125 μm. Toluene was used as an eluent. The final purification was performed by flash chromatography on active coal SKN-2K. The purified solid C_{60} (above 99.8%) was washed with ether and then was sublimed in high vacuum to remove incorporated solvent. For the preparation of iodine-doped fullerenes,[11] a mixture of C_{60} or C_{70} and elemental I_2 was sealed into an evacuated silica glass ampoule and heated for 72 h at 560 K with subsequent slow cooling for 32 h to room temperature. An estimated starting iodine vapor pressure in ampoule was ~10 atm. After cooling, one end of the ampoule was heated at 100 C for half an hour, with another end of it being kept at 78 K to eliminate an excess of unreacted iodine. The elemental analysis on iodine was performed by reductive extraction/titration of iodine from the toluene solution of the doped material with a sodium sulfite water solution and gave the formula $C_{60}I_{2.4}$ and $C_{70}I_2$.

The brominated C_{60} was prepared by modified procedure described in Ref. 12. A mixture of fine powdered C_{60} and liquid bromine (10 mg of C_{60}/1 ml of Br_2) was stirred under nitrogen at room temperature for 5 days. The solid product $C_{60}Br_{24}$ was isolated by evaporation of the excess of bromine in a flow of dry nitrogen at 50 °C.

The chlorinated fullerene samples were prepared by a technique based on the data of Ref. 13. For 6 h, the C_{60} or C_{70} fullerenes were placed into a flow of dry chlorine at 600 K. Thereafter, temperature was lowered to a room level with a rate of 50 K/h and, finally, chlorine was replaced by argon for an hour. The compositions of the prepared samples determined by weight uptake and confirmed by thermogravimetric analysis were found to be $C_{60}Cl_{24}$ (that corresponds to a stoichiometric compound[12]) and $C_{70}Cl_{17}$. The latter should be referred to just as a bulk formula. Real stoichiometry of this compound is not known at present. The samples were obtained in the form of powders of light-yellow ($C_{60}Cl_{24}$) and yellow-brownish ($C_{70}Cl_{17}$) color.

The Raman scattering spectra (RSS) were investigated using a triple spectrometer T64000 Jobin-Ivon equipped with a liquid-nitrogen-cooled charge-coupled device detector and Z-24 Dilor triple spectrometer. The typical spectral resolution was 5 cm^{-1}. The pseudobackscattering configuration was chosen. Nine different lines of a Ar-Kr laser with wavelengths ranging from 468.1 up to 568.1 nm as well as the 632.8 nm line of a He-Ne laser were used for excitation of the RSS. The incident power density at the sample did not exceed 1 $\mathrm{mW/mm}^2$. All the spectra were recorded at room temperature.

Infrared-absorption (IR) spectra were obtained by an IFS-113v Brucker spectrometer. The absorption spectra in the visible region were measured by a DFS-12 spectrometer.

III. TWO TYPES OF BONDING IN HALOGEN-FULLERENE COMPOUNDS

A. Iodine-doped fullerenes: van der Waals C-I bonding

The most clear and evident manifestation of halogen doping is observed in the Raman spectra of $C_{70}I_2$ compounds (Fig. 1). In the RSS of iodine-doped C_{70} crystals, the frequencies and relative intensities of phonon lines corresponding to pure C_{70} remain nearly unchanged by doping. Additionally, in the low-frequency region, a new narrow intense line at 198 cm^{-1} arises. Bearing in mind that the totally-symmetrical vibration frequency of a free I_2 molecule is 213 cm^{-1}, we can assign this low-frequency line to the A_g vibration of the I_2 molecule in $C_{70}I_2$ crystals. For the α phase of iodine-doped C_{70} crystals, the stoichiometric compound corresponds to equal numbers of C_{70} and I_2 molecules.[14] The chemical analysis of the $C_{70}I_2$ samples synthesized and studied in the present paper has shown that they are close to stoichiometric ones. Therefore, these samples are assumed to be perfectly ordered crystals that account for the 198-cm^{-1} line induced by the A_g vibrations of I_2 molecules being narrow.

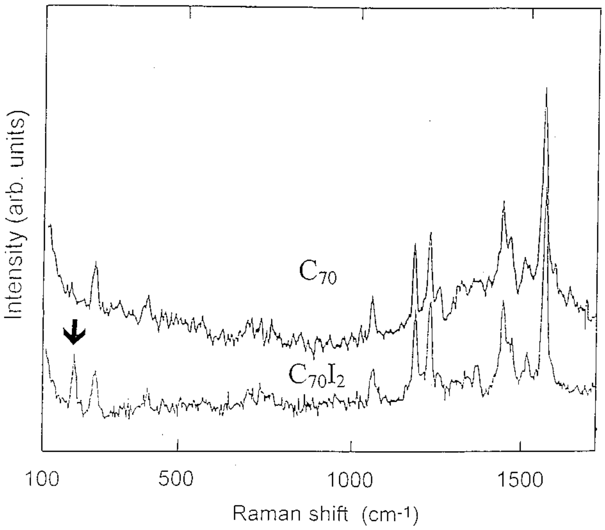

FIG. 1. Raman spectra of C_{70} and $C_{70}I_2$ compounds at $T=300$ K.

The different situation is for the $C_{60}I_{4-x}$ crystals (see Fig. 2). In this system, the stoichiometric compound corresponds to the ratio of 2 molecules of I_2 per C_{60} molecule.[15] Accord-

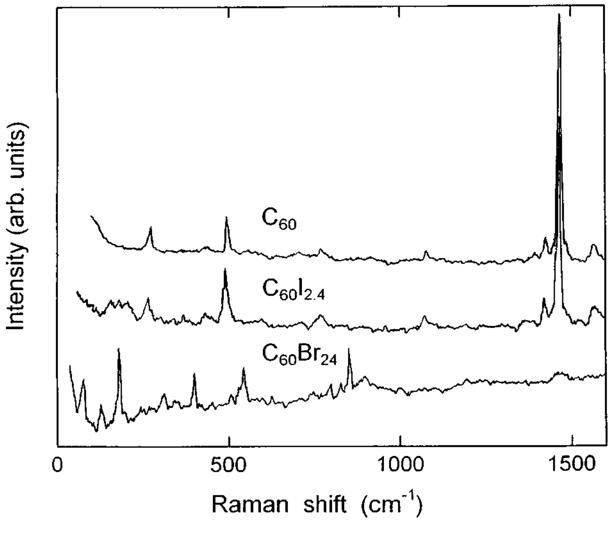

FIG. 2. Raman spectra of C_{60}, $C_{60}I_{2.4}$, and $C_{60}Br_{24}$ compounds at $T=300$ K.

ing to the chemical analysis data, we studied the $C_{60}I_{2.4}$ compound, i.e. the I_2 molecule sublattice was disordered that accounts for a broad band at 165–215 cm^{-1}. This band is formed by the A_g modes of the iodine sublattice which were found to be Raman-active by the group-theory analysis, see Eq. (A3).

We can assume the type of chemical bonding between iodine and carbon atoms if we take into account that the RSS lines corresponding to intramolecular modes in C_{60} and C_{70} nearly do not shift in $C_{60}I_{4-x}$ and $C_{70}I_2$ (with accuracy of $\pm 2\ \mathrm{cm}^{-1}$). The fullerene molecules are more rigid than the I_2 ones which change their interatomic distance I-I in the crystal, resulting in a shift of the A_g-line frequency from the corresponding value ($213\ \mathrm{cm}^{-1}$) of a free I_2 molecule vibrations. Note that in the RSS of the $C_{60}I_{4-x}$ and $C_{70}I_2$ compounds no new lines appeared in the frequency region of C-I vibrations [450–650 cm^{-1} (Ref. 6)] that indicates the absence of C-I bonds. Then we can conclude that C_{60}/C_{70} and I_2 molecules are bound by weak van der Waals forces without charge transfer. This conclusion is supported by the results of calculations of electronic structure made within the CNDO approximation[16] that show very weak interaction between C_{60} ball and iodine molecule I_2. The Wiberg indices of C-C bonds in $C_{60}I_2$ are close to those in undoped fullerene C_{60}. A similar conclusion was made in Ref. 17 when studying the influence of 16 different matrices on the vibrations of I_2, Br_2, and ICl molecules. Only for the I_2-pyridine system was a charge transfer registered.

Thus, we can conclude that the $C_{60}I_{4-x}$ and $C_{70}I_2$ compounds can be considered as quasimolecular crystals formed by two sets of weakly interacting molecules C_{60}/C_{70} and I_2. The vibrational spectra of these compounds are superpositions of C_{60}/C_{70} and I_2 spectra. Our conclusions contradict those of Ref. 2. Indeed, if a charge transfer results in a shift of the C_{60} phonon lines, one could expect the line hardening (in the case of halogen doping) in contrast to a softening observed in the case of a donor doping in $C_{60}M_x$.[3] We have observed no shifts at all. The authors of Ref. 2 observed only an appearance of a very weak line at the low-frequency wing of the intense A_g mode (rather than a shift of this line as a whole) in the xx and yy polarizations (and absent in the zz one). Therefore, the results of Ref. 2 can be hardly considered as an argument in favor of a charge transfer.

B. $C_{60}Br_{24}$ compounds: covalent C-Br bonding

The RSS of $C_{60}Br_{24}$ differ significantly both from C_{60} and Br_2 spectra (Fig. 2). In particular, the line with the frequency of a free Br_2 molecule ($317\ \mathrm{cm}^{-1}$) is absent. Next, in contrast to $C_{60}/C_{70}I_x$ compounds several new lines are observed in the C-Br frequency region (500–700 cm^{-1}) (Ref. 6) that can be connected with C-Br bonds. Most of the observed lines appear to be assigned to totally-symmetric A_g modes which, as a rule, are the most intense lines in the spectra. Therefore, we can assume the formation of C-Br covalent bonds that influences strongly on the vibrational spectra of fullerenes including those in which the Br atoms are involved [$3A_g$, see Eq. (A6) in the Appendix] and other vibrations in which the Br atoms do not participate directly. This assumption is confirmed also by calculations of electronic structure[16] that show the Br atoms to form single covalent bonds with carbon atoms. The comparison of calculated Wiberg indices of C–C bonds indicates that delocalized conjugated bonds in six-fold rings in perfect C_{60} transform into single or double bonds in $C_{60}Br_{24}$. Thus, the $C_{60}Br_{24}$ compound is characterized by a strong covalent bonding C-Br and by a significant redistribution of the electron density at C_{60} molecules with a charge transfer of the order of 0.1 e between neighboring C and Br atoms.[16]

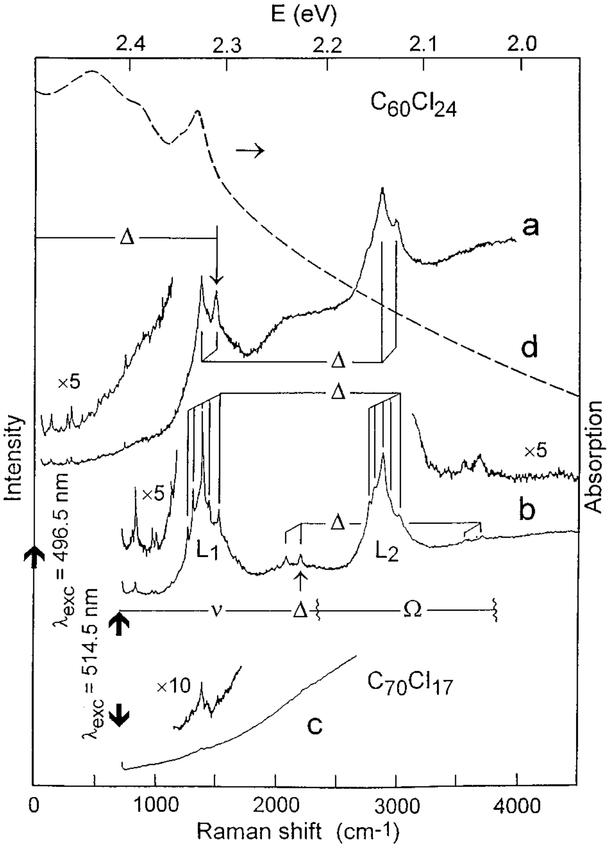

FIG. 3. Secondary luminescence spectra (solid curves) of $C_{60}Cl_{24}$ (a,b) and $C_{70}Cl_{17}$ (c) compounds for $\lambda_{exc}=496.5$ nm (a) and 514.5 nm (b,c) and the absorption spectrum of $C_{60}Cl_{24}$ (d) (dashed line). $T = 300$ K.

Our spectra and their discussion are in general agreement with those in Ref. 1 except for the high-frequency region. The authors of Ref. 1 observed several peaks at 1600–1700 cm^{-1} indicating that substituted aromatic configurations may be present. We have not found any intense Raman lines with frequencies higher than 1500 cm^{-1}.

IV. RESONANCE RAMAN SCATTERING IN $C_{60}Cl_{24}$

A. Interpretation of Raman spectra of $C_{60}Cl_{24}$

The most surprising Raman spectra were obtained when studying the $C_{60}Cl_{24}$ compounds. These spectra differed drastically from the ones discussed above, namely, from the spectra of C_{60}, $C_{60}I_{4-x}$, and $C_{60}Br_{24}$. To interpret these spectra we have to study also IR spectra and the absorption spectra in the visible region.

In Fig. 3, the resonance Raman spectra of $C_{60}Cl_{24}$ ($\lambda_{exc} = 514.5$ and 496.5 nm) are given together with the absorption spectra in absolute energy scale. The Raman spectra of

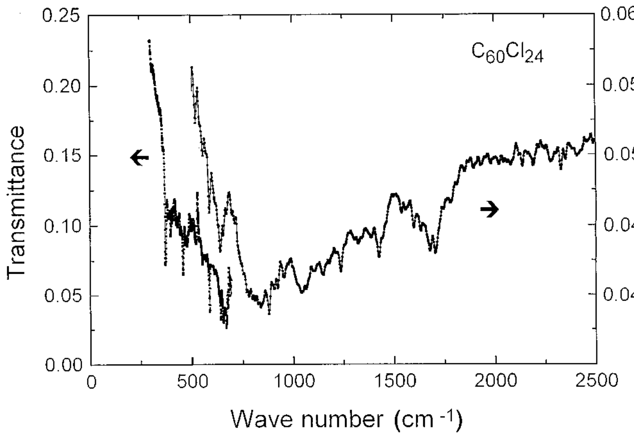

FIG. 4. IR absorption spectra of $C_{60}Cl_{24}$ compound. $T = 300$ K.

$C_{70}Cl_{17}$ ($\lambda_{exc}=514.5$ nm) are also presented for comparison. This figure allows to interpret the observed effects in detail.

In resonance Raman spectra of $C_{60}Cl_{24}$, we can distinguish 4 series of lines and bands labeled by L, ν, Δ, and Ω:

(i) L series consisting of two intense broad bands L_1 and L_2 with energies ~2.33 and 2.14 eV. These bands have similar forms, intensities, and halfwidths ~0.04 eV (~300 cm^{-1}) independent of excitation frequency.

(ii) ν series consisting of relatively narrow (halfwidths 5–30 cm^{-1}) lines. The most intense lines are shifted from the excitation lines by ν=135, 269, 301, 570, 616, 697, 752, 831, and 1385 cm^{-1}. Note that the frequency region of C-Cl bonds is 600–800 cm^{-1}.

Comparing the frequencies of the lines in the Raman and IR spectra of $C_{60}Cl_{24}$ (Figs. 3 and 4) we see that the corresponding vibrations are allowed either in IR or in RSS. This leads to a conclusion that the $C_{60}Cl_{24}$ molecules have an inversion center.

(iii) Δ line with frequency 1508 cm^{-1} (halfwidth ~25 cm^{-1} at λ_{exc}=514.5 nm). We selected this line as a separate group due to several reasons. First, this line is the most intense line in the vibrational spectra of $C_{60}Cl_{24}$ at nonresonant excitation (λ_{exc}=488 nm). Comparing Figs. 2 and 3, one can assume that the 1508 cm^{-1} line in the $C_{60}Cl_{24}$ spectrum is originated from the 1467 cm^{-1} vibration of the C_{60} crystal having the A_g symmetry and being the most intense in the RSS. Besides, the Δ vibration at 1508 cm^{-1} turns out to be a ''key'' one in our interpretation, i.e., its interaction with the electron subsystem determines the effect of repetition of vibrational and luminescence lines in the spectra.

(iv) Ω series consisting of lines with different intensities and halfwidths (10–50 cm^{-1}) shifted by more than 1508 cm^{-1} from the excitation frequency, among them the lines at 2082, 2126, 2207, 2330, 2890, and 3015 cm^{-1}.

Now let us assign each of these four series. The frequency and halfwidth of the L_1 band (~2.33 eV) coincide with those of the 2.33 eV band in the absorption spectrum of the $C_{60}Cl_{24}$ crystal (Fig. 3). The latter line lies below fundamental absorption edge. This band is not induced by defects or impurities in the $C_{60}Cl_{24}$ crystal that follows from the data in Fig. 5 where the absorption spectra of solid $C_{60}Cl_{24}$ as well as its solution in toluene are presented. Really, one can see that this band exists in both systems with its small shift in the case of $C_{60}Cl_{24}$ molecules in the solution relative to a solid phase. Taking into account that the energy of the L_1 band does not depend on the excitation light frequency (Fig. 3) and this band is absent in the anti-Stokes spectral region, we can assign the L_1 band to the luminescence from the electron state at 2.33 eV. As for the L_2 band with energy of 2.14 eV, it should be noted that there is no absorption band in this frequency region.

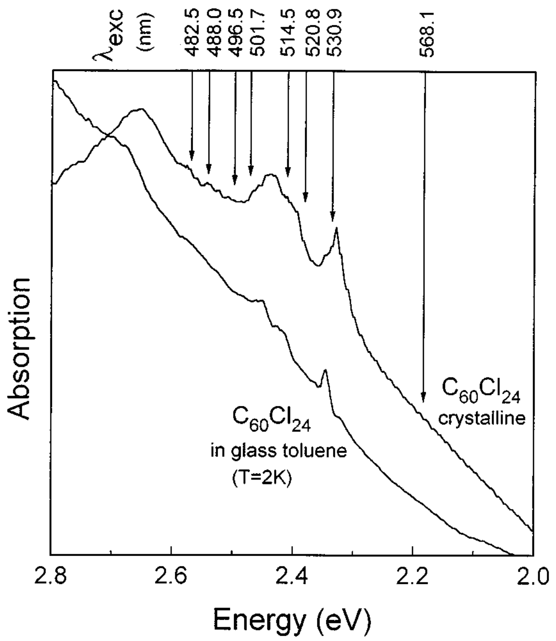

FIG. 5. Absorption spectra of $C_{60}Cl_{24}$ in solid phase ($T = 300$ K) and in glass toluene ($T = 2$ K). Different λ_{exc} of Ar-Kr laser are marked by arrows.

In contrast to the L_1 band, the frequencies of the ν and Δ lines shift when varying the excitation wavelength λ_{exc}. One can observe both Stokes and anti-Stokes components in the spectra, at least for the low-frequency ν lines. Note that the frequencies of ν and Δ lines lie within the range of 100–1600 cm^{-1} that coincides with the phonon frequency range of fullerenes[1,2] and halogen fullerenes (Figs. 1 and 2). This indicates that the ν and Δ lines should be assigned to the Raman scattering by optical phonons in $C_{60}Cl_{24}$.

Figure 3 demonstrates the existence of a strong dependence of the intensities of ν lines on the excitation wavelength λ_{exc} (see the low-frequency part of Raman spectra given in an enlarged scale). In particular, at λ_{exc}=514.5 nm, the intensity of the 135 cm^{-1} line is three times larger than the intensities of the 296 and 301 cm^{-1} lines whereas these three lines have similar intensities at λ_{exc}=496.5 nm.

At last, we discuss the origin of the Ω series of lines as well as of the L_2 band. For all these lines, the following rule holds:

$$\Omega_i = \nu + \Delta, \tag{1}$$

$$\Omega_j = \Delta + \Delta, \tag{2}$$

$$L_1 = L_2 + \Delta, \tag{3}$$

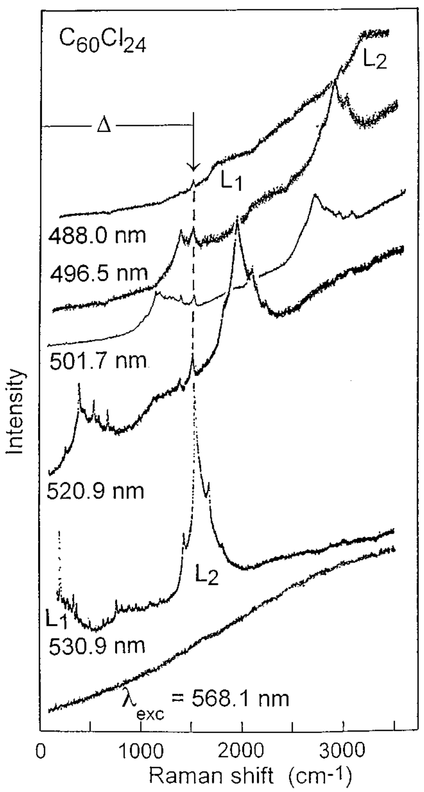

FIG. 6. Secondary luminescence spectra of $C_{60}Cl_{24}$ for different λ_{exc} at $T=300$ K.

where the frequencies ν, Δ, and Ω are taken relative to the frequency of excitation light whereas the frequencies of L_1 and L_2 bands are absolute values. It means that all these spectral features are Δ replicas of phonon spectrum and luminescence L_1 band. The largest shift corresponds to the line $\Omega=3015\ \mathrm{cm}^{-1}=2\Delta$.

B. Resonance behavior of Raman scattering in $C_{60}Cl_{24}$

All main features of the Raman spectra being interpreted, we discuss the general picture of resonance effects in the RSS of $C_{60}Cl_{24}$ compounds based on Figs. 3–6.

Figure 5 presents the absorption spectra of the $C_{60}Cl_{24}$ solid phase and its solution in toluene. The energies of all excitation lines of an Ar-Kr laser used in our experiments are also marked in this figure. One can see that the excitation range (from the blue line at 482.5 nm up to the red line at 568.1 nm) overlaps the whole region of absorption bands in $C_{60}Cl_{24}$ with the line at 530.9 nm coinciding exactly with the absorption line responsible for resonance effects.

In Fig. 6, the transformation of the RSS of $C_{60}Cl_{24}$ when changing the excitation energy $h\nu_{exc}$ within the whole range is presented. In contrast to Fig. 3 where the spectra are shown in absolute energy scale, the relative energy scale (Raman shift, $h\nu_{exc}-h\nu$) is used in Fig. 6. This was made for convenience: in Fig. 3 the luminescence lines (L_1 and L_2) whereas in Fig. 6 the phonon lines (ν,Δ,Ω) do not shift when changing the excitation energy.

When discussing Fig. 6 note that there are no resonance effects in $C_{60}Cl_{24}$ at the light excitation with energies under 2.33 eV (e.g., at $\lambda_{exc}=568.1$ nm). As a result, in the RSS, the only very weak Δ line at 1508 cm^{-1} if any can be observed. When increasing the excitation energy up to the absorption band ($\lambda_{exc}=530.9$ nm), the resonance flareup of phonon spectra is observed. It is accompanied by a repetition of phonon and luminescence lines shifted by the phonon frequency Δ of the most intense line in RSS. These effects are clearly observed within the excitation frequency range $530.9 \geqslant \lambda_{exc} \geqslant 496.5$ nm. At $\lambda_{exc} \leqslant 488.0$ nm, when the condition $h\nu_{exc}-h\Delta>2.33$ eV begins to hold (i.e., the excitation frequency is shifted by a value larger than $\Delta=1508\ \mathrm{cm}^{-1}$ relative to the absorption band), the effect of phonon spectrum repetition disappears. For example, at $\lambda_{exc}=488.0$ nm one can see the only phonon line at 1508 cm^{-1} and two luminescence bands L_1 and L_2 that are weaker than those at resonance conditions.

It should be noted that at resonance conditions, the intensities of all the phonon lines (ν,Δ,Ω) are two orders higher than those in the nonresonance case. The Ω lines are slightly broadened (no more than twice) in comparison with the ν lines. The L_1 and L_2 bands have nearly equal intensities and halfwidths.

The resonance character of the phenomena described above is supported by the absence of such effects in the spectra of $C_{70}Cl_{17}$ (see Fig. 3) that has no peculiarities in the absorption spectra in the investigated excitation range.

V. CONCLUSIONS

The study of phonon states of halogen-fullerene compounds shows a significant difference in their properties. Iodine-doped compounds ($C_{60}I_{4-x}$ and $C_{70}I_2$) can be considered as a quasi-molecular crystal formed by two sets of weakly interacting molecules C_{60} or C_{70} and I_2. The vibrational spectrum of this crystal is a superposition of C_{60}/C_{70} and I_2 spectra. In this compound, the charge transfer is nearly absent. In contrast, the vibrational spectrum of bromide- and chloride-doped compounds differs both from C_{60} (or C_{70}) and Br_2 (or Cl_2) spectra. These compounds are characterized by a strong covalent bonding C-Br, C-Cl, and by a significant redistribution of the electron density at C_{60} molecules. The mutual exclusion of the observed phonon lines in the IR and RSS of $C_{60}Cl_{24}$ allows to conclude that these molecules have an inversion center.

The group-symmetry analysis of phonon symmetry has been performed both for rigid crystals and nonrigid ones with rotating molecules. This analysis shows that halogen atoms (iodine in $C_{60}I_{4-x}$, bromine in $C_{60}Br_{24}$, and chlorine in $C_{60}Cl_{24}$) contribute to Raman-active modes that corresponds to experiments. According to analysis of nonrigid crystals, one can expect the appearance of the rotational fine structure in each of the vibrational modes. This fine structure has not yet been observed in Raman spectra due to low resolution. It will be a subject of future experimental studies.

The phenomenon of resonance Raman scattering in $C_{60}Cl_{24}$ has been investigated in detail. This effect results in a repetition of phonon and luminescence lines and their intensity enhancement. It can be attributed to interaction of the phonon subsystem and electron states with energies 2.3–2.5 eV. We have established that resonance effects are due to intrinsic molecular $C_{60}Cl_{24}$ electronic structure rather than to defects or impurities.

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APPENDIX: GROUP-THEORY ANALYSIS OF PHONON SYMMETRY IN RIGID AND NONRIGID HALOGEN-FULLERENE CRYSTALS

Fullerenes are molecular crystals that exist in several phases depending on various parameters such as temperature, pressure, etc.[18,19] In high-temperature phases, the molecules can rotate[18,19] that makes the phonon spectra of such objects more complicated. In the Appendix, we consider the symmetry of phonons in these crystals both in rigid and nonrigid (with rotating molecules) models. Then we establish a correspondence between the phonon modes in these two cases. This procedure can be easily extended over the symmetry of electron states. Below we consider the symmetry of phonon subsystems in $C_{60}I_4$, $C_{60}Br_{24}$, and $C_{60}Cl_{24}$ crystals.

1. $C_{60}I_4$ crystals

The space group of $C_{60}I_4$ is $C_{3i}^1(P\overline{3})$ (hexagonal Bravais lattice) with 10 sets of C atoms (C1–C10) occupying $6g$ positions (site symmetry C_1) and I atoms occupying $2d(C_3)$ and $3f(C_i)$ positions with fractional occupation numbers.[20]

Using the method of band induced representations of space groups[21] we determined the symmetry of normal vibrations of $C_{60}I_4$ crystals at the symmetry points of the Brillouin zone (BZ). The results are presented in Table I. Table I (and Tables II and III) have the following structure. Column 1 contains the arrangement of atoms over the Wyckoff positions given in column 2 together with their coordinates (in units of primitive translations a_i of direct lattice) and site symmetry groups. Column 3 contains the symbols of those irreducible representations (irreps) of site symmetry groups for these Wyckoff positions according to which the components of local atomic displacements transform. The remaining columns give the labels of induced representations in the k basis, with the symbols of k points (wave vectors), their coordinates (in units of primitive translations b_i of the reciprocal lattice) and their point groups in rows 1–3, respectively, and the indices of small irreps of little groups in the subsequent rows; these determine the symmetries of normal modes. In these Tables, the labeling of the space group irreps is that of Ref. 22, the labeling of the point group irreps is that of Ref. 23, and the site points q are indexed as Wyckoff positions from Ref. 24. Summing the contributions of the atoms in the primitive cell in the full vibrational representation at the Γ point of the BZ (Table I, column 4) one can easily obtain

$$\Gamma = 31\Gamma_1^- + 31(\Gamma_2^+ + \Gamma_3^+) + 34\Gamma_1^- + 34(\Gamma_2^- + \Gamma_3^-)$$
$$= 31A_g + 31({}^1E_g + {}^2E_g) + 34A_u + 34({}^1E_u + {}^2E_u). \tag{A1}$$

The modes A_g and A_u are nondegenerated. The modes described by physically irreducible reps $E_g = {}^1E_g + {}^2E_g$ and $E_u = {}^1E_u + {}^2E_u$ are doubly degenerated. They consist of nondegenerate complex-conjugate pairs and the degeneracy is associated with time inversion. The following vibrations are active in the first-order Raman spectra

$$\Gamma = 31A_g(xx,yy,zz) + 31E_g(xz,yz). \tag{A2}$$

We do not distinguish between intramolecular and intermolecular (translational and librational) modes since the positions of iodine molecule centers are not well defined. Taking in Eq. (A1) only the contributions of iodine atom vibrations, we obtain

$$\Gamma(I) = A_g + ({}^1E_g + {}^2E_g) + 4A_u + 4({}^1E_u + {}^2E_u). \tag{A3}$$

Thus, we can conclude that for the stoichiometric compound there are two Raman-active modes A_g and $E_g = {}^1E_g + {}^2E_g$ induced by the iodine atoms in $2d$ positions only. It should be noted that fractional occupation of $2d$ and $3f$ po-

TABLE I. Phonon symmetry in $C_{60}I_{4-x}$ [space group $C_{3i}^1(P\overline{3})$].

Atoms	q	β	Γ (000) C_{3i}	A $(00\frac{1}{2})$ C_{3i}	K $(\frac{1}{3}\frac{1}{3}0)$ C_3	H $(\frac{1}{3}\frac{1}{3}\frac{1}{2})$ C_3	M $(\frac{1}{2}00)$ C_i	L $(\frac{1}{2}0\frac{1}{2})$ C_i
	$2d$	$a_1(z)$	$1^+,1^-$	$1^+,1^-$	2,3	2,3	$1^+,1^-$	$1^+,1^-$
I1	$(\frac{1}{3}\frac{2}{3}z)$	$e_1(x,y)$	$2^+,2^-$	$2^+,2^-$	1,3	1,3	$1^+,1^-$	$1^+,1^-$
	C_3	$e_2(x,y)$	$3^+,3^-$	$3^+,3^-$	1,2	1,2	$1^+,1^-$	$1^+,1^-$
I2	$3f$ $(\frac{1}{2}0\frac{1}{2})$ C_i	$a_u(x;y;z)$	$1^-,2^-,3^-$	$1^+,2^+,3^+$	1,2,3	1,2,3	$1^+,1^+,1^-$	$1^+,1^-,1^-$
C1–10	$6g$		$1^+,1^-$,	$1^+,1^-$,	1,1,	1,1,	$1^+,1^+$,	$1^+,1^+$,
	(xyz)	$a(x;y;z)$	$2^+,2^-$,	$2^+,2^-$,	2,2,	2,2,	$1^+,1^-$,	$1^+,1^-$,
	C_1		$3^+,3^-$	$3^+,3^-$	3,3	3,3	$1^-,1^-$	$1^-,1^-$

TABLE II. Phonon symmetry in $C_{60}Br_{24}$ and $C_{60}Cl_{24}$ [space group $T_h^3(Fm\overline{3})$].

Atoms	q	β	Γ (000) T_h	X $(\frac{1}{2}\frac{1}{2}0)$ D_{2h}	L $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ C_{3i}	W $(\frac{1}{4}\frac{3}{4}\frac{1}{2})$ C_{2v}
C1	$12h$ $(xy0)$ C_s	$a'(x,y)$	$1^+,2^+,3^+,$ $4^+,4^-,4^-$	$1^+,1^+,1^+,2^+,2^-,2^-,$ $3^+,3^-,3^-,4^+,4^-,4^-$	$1^+,1^+,1^-,1^-,2^+,2^-,$ $2^+,2^-,3^+,3^+,3^-,3^-$	1,1,1,1,1,2, 3,3,3,4,4,4
		$a''(z)$	$1^-,2^-,3^-,$ $4^+,4^+,4^-$	$1^-,1^-,1^-,2^+,2^+,2^-,$ $3^+,3^+,3^-,4^+,4^+,4^-$	$1^+,1^+,1^-,1^-,2^+,2^-,$ $2^+,2^-,3^+,3^+,3^-,3^-$	1,2,2,2,2,2, 3,3,3,4,4,4
C2, C3 Br(Cl)	$24i$ (xyz) C_i	$a(x;y;z)$	$1^+,2^+,3^+,$ $1^-,2^-,3^-,$ $4^+,4^+,4^+,$ $4^-,4^-,4^-$	$1^+,1^+,1^+,1^-,1^-,1^-,$ $2^+,2^+,2^+,2^-,2^-,2^-,$ $3^+,3^+,3^+,3^-,3^-,3^-,$ $4^+,4^+,4^+,4^-,4^-,4^-$	$1^+,1^+,1^+,1^+,1^-,1^-,1^-,1^-,$ $2^+,2^+,2^+,2^+,2^-,2^-,2^-,2^-,$ $3^+,3^+,3^+,3^+,3^-,3^-,3^-,3^-,$	1,1,1,1,1,1, 2,2,2,2,2,2, 3,3,3,3,3,3, 4,4,4,4,4,4

sitions by iodine atoms effects on the modes involving the iodine atoms given by Eq. (A3) whereas the intramolecular modes of C_{60} appear to be nonperturbated.

2. $C_{60}Br_{24}$ and $C_{60}Cl_{24}$ crystals

The symmetry of $C_{60}Br_{24}$ crystals is low $C_{3i}^1(P\overline{3})$ (hexagonal Bravais lattice) (Ref. 12) but the intrinsic crystal structure is close to the structure with the idealized maximal symmetry $T_h^3(Fm\overline{3})$ [face-centered cubic (fcc) lattice]. Note that both lattices have an inversion center. In the hexagonal lattice 10 sets of carbon atoms (C1–C10) and 4 sets of Br atoms (Br1–Br4) occupy $6g$ positions (site symmetry C_1). In the fcc lattice 12 carbon atoms (C1) occupy $12h$ position (C_s) and two sets of carbon atoms (C2,C3) and Br atoms occupy $24i$ positions (C_1). There are strong grounds for believing that $C_{60}Br_{24}$ and $C_{60}Cl_{24}$ crystals are isostructural[25] and all results obtained for $C_{60}Br_{24}$ are valid for $C_{60}Cl_{24}$ too. This assumption is also supported by the experiments made in the present paper that show the existence of an inversion center in $C_{60}Cl_{24}$.

The results of the symmetry analysis are presented in Tables II and III. For the idealized fcc lattice, we can write down (Table II) the full vibrational rep at the Γ point

$$\begin{aligned}\Gamma &= 11\Gamma_1^+ + 11(\Gamma_2^+ + \Gamma_3^+) + 31\Gamma_4^+ + 10\Gamma_1^- + 10(\Gamma_2^- + \Gamma_3^-)\\ &\quad + 32\Gamma_4^-\\ &= 11A_g + 11({}^1E_g + {}^2E_g) + 31F_g + 10A_u + 10({}^1E_u + {}^2E_u)\\ &\quad + 32F_u. \qquad (A4)\end{aligned}$$

The modes A_g and A_u are nondegenerated, whereas those with the symmetry F_g and F_u are triply degenerated. The vibrations described by physically irreducible reps $E_g = {}^1E_g + {}^2E_g$ and $E_u = {}^1E_u + {}^2E_u$ are doubly degenerated. The Raman-active modes are given by

$$\Gamma = 11A_g(xx,yy,zz) + 11E_g(xx,yy,zz) + 31F_g(xy,xz,yz). \qquad (A5)$$

Knowing the positions of centers of molecules, we also determined the symmetry of intermolecular translational ($\Gamma_{\mathrm{tr}} = F_u$) and librational ($\Gamma_{\mathrm{lib}} = F_g$) modes. These modes should manifest themselves at the low-frequency region.

The contribution of Br atoms is also easily obtained,

$$\Gamma(\mathrm{Br}) = 3A_g + 3E_g + 9F_g + 3A_u + 3E_u + 9F_u. \qquad (A6)$$

From Eq. (A6) one can see that the bromine atomic displacements induce 3 A_g modes that usually are the most intense in the Raman spectra.

The real hexagonal structure can be obtained from the idealized fcc one by a small perturbation that reduces the symmetry. Within the model of a rigid crystal, this leads to a splitting of F_g and F_u modes $F_{g,u} \rightarrow A_{g,u} + ({}^1E_{g,u} + {}^2E_{g,u})$. As a result, from Table III we obtain the full vibrational rep at the Γ point

$$\begin{aligned}\Gamma &= 42[\Gamma_1^+ + (\Gamma_2^+ + \Gamma_3^+) + \Gamma_1^- + (\Gamma_2^- + \Gamma_3^-)]\\ &= 42[A_g + ({}^1E_g + {}^2E_g) + A_u + ({}^1E_u + {}^2E_u)], \qquad (A7)\end{aligned}$$

where the correspondence between irreps of T_h^3 and C_{3i}^1 at the Γ point is the following:

TABLE III. Phonon symmetry in $C_{60}Br_{24}$ and $C_{60}Cl_{24}$ [space group $C_{3i}^1(P\overline{3})$].

Atoms	q	β	Γ (000) C_{3i}	A $(00\frac{1}{2})$ C_{3i}	K $(\frac{1}{3}\frac{1}{3}0)$ C_3	H $(\frac{1}{3}\frac{1}{3}\frac{1}{2})$ C_3	M $(\frac{1}{2}00)$ C_i	L $(\frac{1}{2}0\frac{1}{2})$ C_i
C1-10 Br(Cl)1–4	$6g$ (xyz) C_1	$a(x;y;z)$	$1^+,1^-,$ $2^+,2^-,$ $3^+,3^-$	$1^+,1^-,$ $2^+,2^-,$ $3^+,3^-$	1,1, 2,2, 3,3	1,1, 2,2, 3,3	$1^+,1^+,$ $1^+,1^-,$ $1^-,1^-$	$1^+,1^+,$ $1^+,1^-,$ $1^-,1^-$

TABLE IV. Reps of $[T_r]$ subduced by irreps of $[O]\times[T]$.

$[O]\times[T]$	$[T_r]$
(a_1,a)	a
$[a_1,e^{(1)}]$	$e^{(1)}$
$[a_1,e^{(2)}]$	$e^{(2)}$
(a_1,f)	f
(a_2,a)	a
$[a_2,e^{(1)}]$	$e^{(1)}$
$[a_2,e^{(2)}]$	$e^{(2)}$
(a_2,f)	f
(e,a)	$e^{(1)}e^{(2)}$
$[e,e^{(1)}]$	$ae^{(2)}$
$[e,e^{(2)}]$	$ae^{(1)}$
(e,f)	$2f$
(f_1,a)	f
$[f_1,e^{(1)}]$	f
$[f_1,e^{(2)}]$	f
(f_1,f)	$ae^{(1)}e^{(2)}2f$
(f_2,a)	f
$[f_2,e^{(1)}]$	f
$[f_2,e^{(2)}]$	f
(f_2,f)	$ae^{(1)}e^{(2)}2f$

$$\begin{gathered} A_{g,u}\rightarrow A_{g,u}\,; \\ {}^{1,2}E_{g,u}\rightarrow {}^{1,2}E_{g,u}\,; \\ F_{g,u}\rightarrow A_{g,u}+[{}^{1}E_{g,u}+{}^{2}E_{g,u}]. \end{gathered} \tag{A8}$$

Therefore, in the first-order Raman spectra of hexagonal $C_{60}Br_{24}$, there are allowed 9 additional A_g modes induced by the vibrations of Br atoms. However the lines in the RSS corresponding to these modes should be weak since they are due to small distortion of a fcc lattice.

3. Nonrigid crystal with rotating molecules

The symmetry of the idealized structure of the crystal $C_{60}Br_{24}$ ($C_{60}Cl_{24}$) with internal rotation of the $C_{60}Br_{24}$ ($C_{60}Cl_{24}$) molecules (such crystals are called nonrigid) may be described by the permutation-inversion group[21]

$$[G_{\mathrm{PI}}]=[O_h^5]\times\{T\},\quad \{T\}=[T]\times[T]\times[T]\times\cdots, \tag{A9}$$

where the symbol $[G]$ is used for permutation-inversion group isomorphic with a point or space group G. A site group of a rotating molecule $C_{60}Br_{24}$ in the group $[G_{\mathrm{PI}}]$ is

$$[S_{\mathrm{PI}}]=[O_h]\times[T]=[O]\times[T]\times[C_i]. \tag{A10}$$

When the rotation of the molecules is frozen $[G_{\mathrm{PI}}]$ and $[S_{\mathrm{PI}}]$ are reduced to $[T_h^3]$ and $[T_h]$, respectively.

To satisfy the principle of symmetry with respect to the permutations of identical carbon and bromine nuclei the wave functions of rotating molecules have to transform according to the unity representation of the subgroup $[T]\subset[S_{\mathrm{PI}}]$.[10] Let us develop $[S_{\mathrm{PI}}]$ in terms of left cosets with respect to $[T_h]$,

$$[S_{\mathrm{PI}}]=\sum_{[g]}[g][T_h]. \tag{A11}$$

The permutation-inversion element $[g]$ transfers the molecule in rigid crystal into the configuration that is separated from the initial one by an insurmountable barrier. Every librational state of the molecule induces 23 more states that are not realized because of the insurmountability of the barriers. When the barriers become surmountable the molecules begin to rotate and all these states become realizable and may be classified according to the irreps of the group $[S_{\mathrm{PI}}]$. Table IV contains the irreps of the group $[T_r]$ (subgroup of the site symmetry group of the molecule in the rigid crystal) subduced by the irreps of the group $[O]\times[T]$. With the help of Frobenius reciprocity theorem one finds that for example the lowest and the first excited librational states of the molecule (the irreps a_g and f_g of the group $[T_h]$) induce the states of symmetry $(a_1,a)_g$, $(a_2,a)_g$, $[e,e^{(1)}]_g$,$[e,e^{(2)}]_g$, $(f_1,f)_g$, $(f_2,f)_g$ and $(a_1,f)_g$, $(a_2,f)_g$, $2(e,f)_g$, $(f_1,a)_g$, $[f_1,e^{(1)}]_g$, $[f_1,e^{(2)}]_g$, $2(f_1,f)_g$, $(f_2,a)_g$, $[f_2,e^{(1)}]_g$, $[f_2,e^{(2)}]_g$, $2(f_2,f)_g$, respectively.

The mentioned above principle of symmetry imposes the restrictions on the symmetry of the possible excited states of the molecule (electronic, vibrational, rotational, and combined). In particular, the most part of the vibrational and electronic molecular excitations can exist in crystal only as combined (rovibrational, vibronic, or rovibronic).[10]

The internal ground state of the crystal is approximately a product of ground states of all the molecules. The lowermost excited states are described by the Bloch sums of products of the molecular wave functions where only one molecule is in the excited states and the others are in the ground states. These functions transform according to the irreps of the group $[G_{\mathrm{PI}}]$ formally coinciding with those of the group O_h^5.

Let us compare the symmetry analyses of crystal states in the frame of the groups $[T_h^3]$ and $[G_{\mathrm{PI}}]$ of rigid and nonrigid crystals. The wave functions of internal states (without the wave functions describing the translational and rotational motion of the crystal as a whole) are classified according to the irreps of the groups T_h^3 and O_h^5, respectively. The phonons corresponding to intramolecular vibrations do not exist in a nonrigid crystal. In the latter intramolecular vibrations are always accompanied by the rotational excitations. Therefore the vibrational spectra of nonrigid crystals have always the rotational structure which contributes to the form of vibrational lines.

The symmetry of the surroundings cannot split the degeneracy of the intramolecular vibrations on condition that there is a rotation of molecules. One may say the same about the electronic intramolecular states.

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