

Size effects and migration of matrix-isolated Hg_2Cl_2 molecules

B. S. Zadokhin, M. F. Limonov, Yu. F. Markov, and V. P. Petranovskii
A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR, Leningrad

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The Raman scattering spectra of Hg_2Cl_2 molecules isolated in the cavities of zeolites reveal a manifestation of translational vibrations due to a lowering of the dimensionality of the entities in comparison with 3D crystals. Effects of a migration and an ordering of Hg_2Cl_2 molecules in zeolite matrices have also been observed.

Calomel, Hg_2Cl_2 , is a convenient compound for studying how size effects influence the vibrational spectra of solids. It has a simple crystal structure and some very intense Raman scattering spectra. At $T = 300$ K, Hg_2Cl_2 crystals have a body-centered tetragonal lattice of symmetry D_{4h}^{17} , with one linear Cl–Hg–Hg–Cl molecule per primitive cell. The vibrational spectra of first and second orders of bulk Hg_2Cl_2 single crystals have been studied in detail by Raman scattering^{1–3} and IR spectroscopy.^{4,5} For example, four vibrations are allowed theoretically and have been observed experimentally (Fig. 1) in the first-order Raman spectra of Hg_2Cl_2 crystals: two doubly degenerate vibrations of symmetry $E_g(zx, zy)$ (ν_1 is an intermolecular librational vibration, and ν_2 is a deformation vibration) and two completely symmetric valence vibrations of symmetry $A_{1g}(xx, yy, zz)$ (ν_3 corresponds to Hg–Hg displacements, and ν_4 to Hg–Cl displacements).

The transition from 3D calomel crystals to 1D crystals (chains of Hg_2Cl_2 molecules) and zero-dimensional entities (essentially isolated Hg_2Cl_2 molecules) was made by introducing these molecules in inert matrices of zeolites: skeletal aluminosilicate structures with a strictly periodic system of channels or cavities. To distinguish possible effects stemming from the presence of the matrix, we used zeolites of three types: NaA, NaX, and NaM, whose structures are described in detail in Ref. 6. The zeolite NaA has a cubic symmetry and nearly spherical cavities, 11.4 Å in diameter, connected by 4.2-Å windows. The zeolite NaX has a diamond lattice with cavities 12–13 Å in diameter, connected by windows 8–9 Å in size. The concentration of the cavities of these zeolites is $\approx 5 \times 10^{20} \text{ cm}^{-3}$. The zeolite NaM has a system of parallel channels which are approximately cylinders ≈ 7 Å in diameter, with a length limited by the dimensions of the crystal. The zeolites (we used a powder consisting of synthesized single crystals 20–100 μm in size) were filled with the calomel through the adsorption of Hg_2Cl_2 molecules from the gas phase. The size of the Hg_2Cl_2 molecule is 10.9 Å. The filling was carried out to the extent which would result in 1 molecule per cavity.

1. Intramolecular vibrations. The Raman spectra of the zeolite- Hg_2Cl_2 samples were studied on a DILOR Z-24 Raman spectrometer with an Ar laser over the tem-

perature range 77–600 K. Figure 1 shows some resulting spectra; the frequencies are listed in Table I. Taking into account the clear analogy among all four spectra in Fig. 1, we can confidently interpret three lines in each of the Raman spectra of the zeolite- Hg_2Cl_2 systems as corresponding to vibrations ν_2 – ν_4 of crystalline calomel (Table I). The Raman spectrum of the zeolites themselves is extremely faint and cannot be seen at the intensity scale in Fig. 1. It follows from Table I that the frequencies of the Hg_2Cl_2 molecules isolated in these three matrices (with different spherical cavities and with cylindrical cavities) are shifted identically with respect to the frequencies of Hg_2Cl_2 single crystals: ν_2 and ν_3 decrease, while ν_4 increases. The case $\text{NaM-Hg}_2\text{Cl}_2$ is particularly important. In this case the molecule is in an external force field, which can be treated as cylindrically symmetric in a first approximation, so it has a minimal effect on the valence vibrations, i.e., on the displacements of atoms along the axis of the molecules. We can therefore assume that the frequencies found (the average values are $\nu_2 \approx 110 \text{ cm}^{-1}$, $\nu_3 \approx 162 \text{ cm}^{-1}$, and $\nu_4 \approx 310 \text{ cm}^{-1}$) are close to the frequencies of the free Hg_2Cl_2 molecule, which have not previously been determined, either experimentally or theoretically. Furthermore, the very fact that experimental vibrations corresponding to Hg–Hg and Hg–Cl bonds are observed in these data answers in the affirmative the question (not previously resolved^{7,8}) of whether an individual Hg_2Cl_2 molecule is stable.

2. Size effects in low-frequency Raman spectra. Figure 2 shows Raman spectra of zeolite- Hg_2Cl_2 samples in the Stokes and anti-Stokes parts of the spectrum. The low level of scattered light in the spectrometer made it possible to study the Raman spectra down to extremely low frequencies, $\approx 5 \text{ cm}^{-1}$, and to distinguish three low-frequency

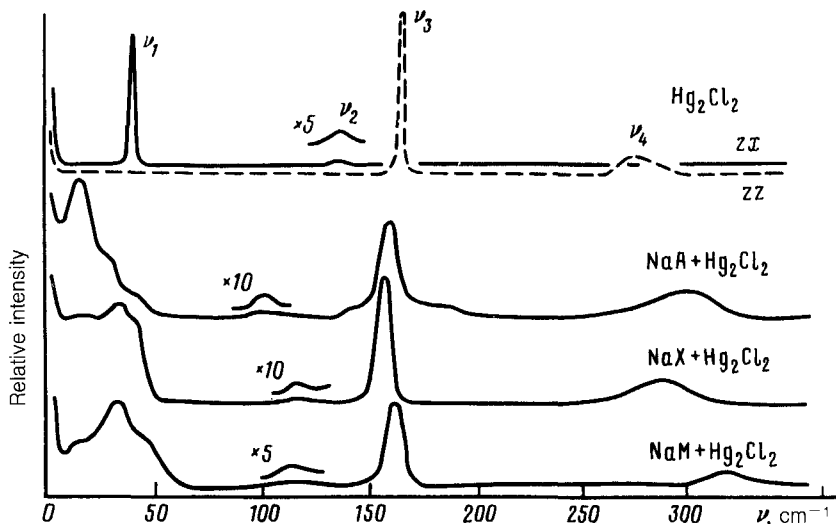


FIG. 1. Polarized Raman spectra of Hg_2Cl_2 single crystals and of zeolite- Hg_2Cl_2 systems at $T = 300 \text{ K}$.

TABLE I. Frequencies of the first-order Raman spectra of Hg_2Cl_2 single crystals and of zeolite- Hg_2Cl_2 systems, in units of reciprocal centimeters.

System	ν_1	ν_2	ν_3	ν_4
Hg_2Cl_2	40	137	167	275
$\text{NaA} + \text{Hg}_2\text{Cl}_2$	15, 30, 41	98	141, 161, 179 or 162	300
$\text{NaX} + \text{Hg}_2\text{Cl}_2$	15, 35, 41	116	158	294
$\text{NaM} + \text{Hg}_2\text{Cl}_2$	16, 34, 46	113	164	320

lines in each case (Table I). In the first-order Raman spectra of crystals, in contrast, there is only a single intense narrow line in this part of the spectrum, at $\nu_1 = 40 \text{ cm}^{-1}$, with a half-width $\Delta\nu_1 \approx 1.5 \text{ cm}^{-1}$. That line corresponds to an intermolecular librational vibration. Working from a study of the temperature dependence of the low-frequency lines and the fact that the intensities of these lines are comparable to those of the lines corresponding to intramolecular vibrations of zeolite- Hg_2Cl_2 (Fig. 1), we conclude that they belong to the first-order Raman spectrum.

The most probable interpretation of these lines is that they are associated with translational and orientational vibrations of Hg_2Cl_2 molecules with respect to the zeolite matrix or with respect to each other. In an ordered bulk crystal, vibrations of this type would be acoustic and would be forbidden by the momentum selection rules in the first-order Raman spectra. As the dimensionality is lowered, however, i.e., as we go from a 3D crystal to an ensemble of weakly interacting or totally isolated molecules, the "crystal" selection rules are violated, and it becomes possible to see these vibrations in the first-order Raman spectra. The two lowest-frequency lines, at $\approx 15 \text{ cm}^{-1}$ and 30 cm^{-1} , may be due to transverse and longitudinal translational vibrations

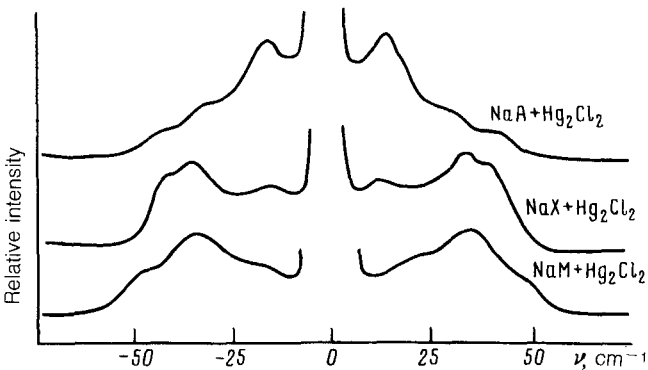


FIG. 2. Low-frequency Raman spectra of zeolite- Hg_2Cl_2 systems in the Stokes and anti-Stokes parts of the spectrum at $T = 300 \text{ K}$.

of the molecules, while the fainter line at $\approx 40 \text{ cm}^{-1}$ may be due to orientational vibrations. Included in the latter category are a rocking of molecules similar to the crystal librational vibrations ν_1 .

3. Migration of Hg_2Cl_2 molecules through the zeolite matrices. Ordering effect.

Let us examine some qualitative changes in the Raman spectra of the zeolite- Hg_2Cl_2 systems which occur under time-varying conditions (a change in the temperature of the sample or a change in the power of a probing laser beam). First, as the laser power is gradually raised from 10 to 100 mW (the beam diameter at the sample was $\sim 100 \mu\text{m}$), all four narrow lines corresponding to the spectrum of bulk Hg_2Cl_2 samples appear in the Raman spectra of all the zeolite- Hg_2Cl_2 systems, and they increase in intensity. Figure 3a–3c demonstrates this intensification of the crystal line $\nu_3 = 167 \text{ cm}^{-1}$ in the vicinity of the $\nu_3 = 158 \text{ cm}^{-1}$ vibration of the NaX- Hg_2Cl_2 system. The appearance of crystal lines is linked with the emergence of some of the Hg_2Cl_2 molecules at the surface of the zeolite single crystals. A simple heating of the samples fails to cause a similar transformation of the spectra; it causes simply an overall lowering of the intensity of the zeolite- Hg_2Cl_2 Raman spectrum, associated with an escape of molecules from the matrix without a pinning at the surface. As the laser power is lowered further, the shape of the spectrum corresponding to Fig. 3c remains essentially the same, but if this sample is heated to $T \approx 150^\circ\text{C}$, the Raman spectrum reverts to its original shape (3D). In other words, an inverse adsorption of Hg_2Cl_2 molecules occurs.

Another effect was observed, but only in the NaA- Hg_2Cl_2 system. Immediately after the synthesis of this system, a triplet was observed near the ν_3 vibration in the Raman spectrum (Fig. 3e and Table I). This triplet can be linked with three different

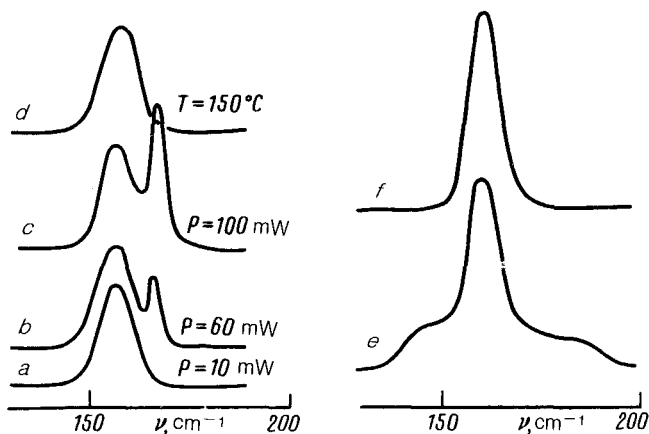


FIG. 3. Transformation of the Raman spectrum near the ν_3 vibration under time-varying conditions. a–c—NaX- Hg_2Cl_2 , with increasing laser power; d—NaX- Hg_2Cl_2 , after heating to $T = 150^\circ\text{C}$; e, f—NaA- Hg_2Cl_2 , before (e) and after (f) heat treatment. The intensities of all spectra have been normalized to their initial values.

equilibrium positions of the Hg_2Cl_2 molecules in the cavities of the NaA matrix. Later, however, in the course of several heating and cooling cycles, the spectrum gradually changed, and the triplet ultimately transformed into a single symmetric line, with a frequency $\nu_3 = 162 \text{ cm}^{-1}$ (Fig. 3f). In subsequent experiments, there was no further change in the shape of this line. Consequently, all the molecules went into the one stablest equilibrium position; as a result, an ordered superstructure of Hg_2Cl_2 molecules probably arose in the zeolite matrix.

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