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An Electron Diffraction Study of the Molecular Structures of PrI_3, NdI_3, GdI_3 and LuI_3

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In recent years the interest for studies of rare earth halides by different physical techniques has increased. However, very little is known concerning the frequencies of vibration and molecular geometries of this class of compounds.

In infrared spectra of the trifluorides of La, Ce, Nd, Eu, Gd, Tb, Ho, Yb and Lu isolated in solid argon matrix [1] four absorption bands have been observed. On the basis of selection rules the pyramidal geometry of all molecules studied was assumed. In another study [2] infrared spectra of the trifluorides of La, Ce, Pr, Nd, Sm and Eu isolated in solid argon, krypton and nitrogen matrices were reported; by contrast, these molecules were assigned a planar configuration.

Electric deflection studies on molecular beams of the lanthanide trifluorides have been carried out [3]. Substantial refocussing, indicative of pyramidal geometry, has been observed for LaF_3, GdF_3 and LuF_3. Weaker refocussing was present for other molecules, barely above the noise level, thus indicating the molecules to be planar or slightly pyramidal.

No conclusive evidence about the molecular geometry has been gained from infrared studies of the neodymium halides in gaseous phase at 1200 °C [4] and trichlorides of La, Gd and Lu in the matrix [5]. The electron diffraction data on LaX_3 and NdX_3 (X is F, Cl, Br and I) [6] did not contribute much to the discussion of rare-earth halide structures as the molecular geometry in this early study cannot be considered to be unambiguously established.

However, recently started systematic up-to-date electron diffraction studies of the molecular structures of some rare earth halides (for summary see [7]) showed the effective configurations of all molecules studied to be pyramidal with a central atom valence angle of 110–115°. The pyramidal structure of these molecules is to be expected also on the basis of valence state energies calculations [8].

In the present investigation the results of the molecular structure study of PrI_3, NdI_3, GdI_3 and LuI_3 by electron diffraction are reported.

Experimental

The samples were prepared from elements of high purity by the method described in [9]. The predominant species among all substances was assumed to be the monomer [10]. The electron diffraction patterns were taken with the improved EG-100M Moscow University apparatus [11] at a nozzle temperature (in K) of 1050 (PrI_3), 1070 (NdI_3), 1060 (GdI_3) and 1015 (LuI_3). The uncertainty or temperature measurements is estimated at 20–30°. The other experimental conditions were: accelerating voltage ~40 kv, camera distances $L_1 \sim 48$ cm and $L_2 \sim 19$ cm. The high temperature radiation-type nozzle system [12] was used for the evaporation of the samples.

The electron wavelength and its uncertainty (0.12%) were calibrated against the ZnO polycrystal diffraction patterns.

After the usual reduction of each set of data the total intensities I(s) were obtained in the range s = 2.2–21.4 $Å^{-1}$. The manually drawn background B(s) was used to convert the I(s) curves into a reduced molecular intensity function sM(s) by means of the relationship $sM(s) = s[I(s) - B(s)]/B(s)$.

The least-squares refinement program [13] adapted for the BESM-6 computer of Moscow University Computing Center was used with a diagonal weight matrix. All internuclear distances (*r*) and mean amplitudes of vibration (*l*) were refined simultaneously and independently. The initials of the disdistance parameters were taken from the radial distribution curve and those of the amplitudes were estimated on the basis of measured *l* values in other rare earth trihalides [7].

At the early stage of analysis the preliminary refinement was carried out using two camera distance intensity curves separately. Finally, both curves were applied for the refinement simultaneously provided each curve yielded the parameters consisting within the experimental uncertainty.

In calculations of $sM_{theor}(s)$ Strand's computed elastic and inelastic atomic scattering factors were applied because from known International Tables [14] these factors for rare earth elements are not available.

In the course of structure analysis small alterations in initial backgrounds have been introduced which did not shift the structure parameters, however, but substantially lowered the agreement factor R_f. The final R_f values for all molecules studied were in the range 5–8%. As an example the sM(s) curve for the PrI_3 molecule is presented in Fig. 1.

A manual procedure of the background drawing was complemented by computer calculated backgrounds based on spline functions [15, 16], which

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TABLE I. Molecular Parameters (Å) for Rare Earth Triiodides with Estimated Uncertainties.[a]

Molecule	Temperature (K)	r_g (Ln–I)	l (Ln–I)	r_g (I–I)	l (I–I)	$<_g$I–Ln–I[b]
PrI_3	1050	2.904(6)	0.113(4)	4.835(57)	0.448(45)	112.7 ± 2.2
NdI_3	1070	2.881(5)	0.100(4)	4.772(48)	0.397(35)	111.8 ± 1.8
GdI_3	1060	2.841(5)	0.100(4)	4.596(57)	0.416(40)	108.0 ± 2.0
LuI_3	1015	2.771(6)	0.106(6)	4.660(51)	0.339(30)	114.5 ± 2.1

[a] Parenthesized quantities are total errors. For the distances they are estimated by the relationship $\sigma^2 = \sigma_{syst}^2 + (2.5\sigma_{ls})^2$ where σ_{syst} = 0.17% a distance. The other parameter error was estimated at $3\sigma_{ls}$. [b] r_g distance parameters were used in obtaining the angles.

TABLE II. Vibrational Frequencies (in cm^{-1}) for the Trifluorides and Trichlorides of La, Nd, Gd and Lu.[a]

Molecule	Matrix	ν_1	ν_2	ν_3	ν_4	Ref.
LaF_3	Ar	513.0	83	479.0	121	[1]
$LaCl_3$	Xe	(260)	52	300	74	[5]
NdF_3	Ar	529.7	87	503.7	119	[1]
	Ar	–	86	502	118	[2a]
$NdCl_3$	gas phase	349	177	306	120	[4]
GdF_3	Ar	544.7	100	519.2	133	[1]
$GdCl_3$	Xe	(270)	53	318	82	[5]
LuF_3	Ar	569.6	112	552.2	144	[1]
$LuCl_3$	Xe	(315)	60	331	88	[5]

[a] Parenthesized values are the frequencies of vibration estimated in [5].

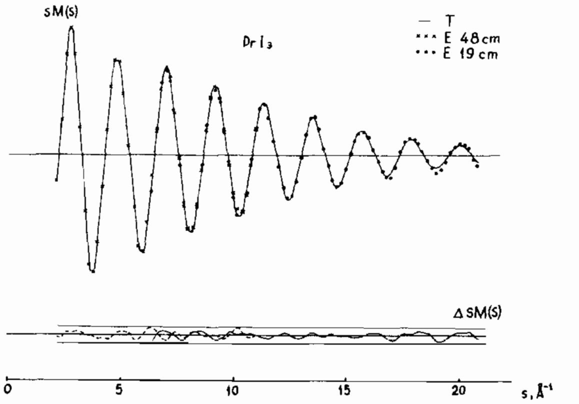

Figure 1. Experimental (E) and theoretical (T) molecular intensities. The 2σ confidence limit is indicated.

led to identical results. The final structure results in terms of r_g and l parameters are given in Table I.

Discussion

The molecular parameter r_g(Nd–I) = 2.881 ± 0.004 Å obtained in the present investigation differs considerably from that found previously [6] (r(Nd–I) = 2.94 ± 0.03 Å). On the other hand, all Ln–I distances are close to the estimates made [17] on the basis of orbital radii of atomic cores and triply charged Ln ions radii.

The data presented in Table I show the effective configuration (r_g structure) of all LnI_3 molecules studied to be pyramidal. For establishing the equilibrium configuration symmetry the vibrational corrections based on spectral data are necessary. However, recently reported vibrational frequencies for neodymium halides [4] seem unsatisfactory as they apparently contradict the smooth regular trend for the frequencies in rare earth trihalide series as may be seen from Table II. In this Table the spectral data for rare earth trichlorides and some trifluorides are presented. It should be pointed out that the ν_2 and ν_4 values for $NdCl_3$ [4] are even higher than those for NdF_3 [1]. Moreover, the neodymium halide frequencies are found to contrast with results of paper [2b] where the general relationship $\nu_2 < \nu_4$ seems to be firmly established. An additional evidence for the inconsistency of the set of vibrational frequencies (cm^{-1}) for NdI_3 reported in [4] (ν_1 = 182, ν_2 = 98, ν_3 = 141, ν_4 = 72) provides the calculation of amplitudes of vibration: l_{calc}(Nd–I) = 0.131 Å and l_{calc}(I–I) = 0.190 Å. These values strongly disagree with electron diffraction values obtained (see Table I).

At the authors' request N.I. Giricheva from Ivanovo Institute of Chemical Technology estimated the frequencies of vibration of PrI_3. In her calculation the trends in vibrational frequencies and force constants in the series of rare earth element trihalides (and other elements of the 3rd group) were used. This calculation yielded the following set of frequencies (cm^{-1}): ν_1 = 135 ± 10, ν_2 = 26 ± 3, ν_3 = 157 ± 20, ν_4 = 39 ± 3. Using these values the r_α parameters and amplitudes of vibration were computed by the program [18]. The results obtained [l_{calc}(Pr–I) = 0.127 Å and l_{calc}(I–I) = 0.446 Å favourably agree with the experiment (see Table I). Average value of bond angle made of r_α parameters turned out to be 116. 3 ± 2.2°. Therefore, on the basis of r_α structure an inference could be made that within the harmonic approximation the equilibrium molecular geometry of PrI_3 (and probably of other iodides studied) is pyramidal.

It should be noted, however, that this conclusion on equilibrium molecular geometry could not be considered fully unambiguous. Namely, the anharmonicity in angle bending vibration may seriously affect the angle parameter. Particularly, for molecules with relatively low frequencies of bending vibration (such seems to be the case for many molecules studied here) the barrier separating two equivalent minima at pyramidal configurations on the potential energy curve may be rather low resulting in the large amplitude motion. Therefore, the ignorance of this effect may be one of the largest sources of uncertainty in the experimental data interpretation. In addition, in some molecules the influence of low lying electronic states causing vibronic interactions seems worth considering. This calls for additional evidence from other sources. One may hope that combined use of different experimental techniques and theoretical approaches will make it possible to ultimately solve the structural and other problems of rare earth halides.

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