

## On the Crystal Structures of the High-temperature Phases of Rubidium Nitrate, Cesium Nitrate, and Thallium Nitrate

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The crystal structures of the high-temperature forms of  $\text{RbNO}_3$ ,  $\text{CsNO}_3$ , and  $\text{TlNO}_3$  have been reconsidered. The structures are suggested to be different from those implied by previous models. Observed transition entropies are compared with calculated values of the orientational entropy obtained for the high-temperature phases of  $\text{RbNO}_3$  in a similar way as done recently for  $\text{KNO}_3$ -I and  $\text{NaNO}_3$ -I.

**M**etal nitrates exhibit frequently a great variety of phase transitions in the solid state. Structural problems of the high-temperature forms of nitrates have recently been reviewed by Newns and Stavelly.<sup>1</sup>

Polymorphic properties of  $\text{RbNO}_3$ ,  $\text{CsNO}_3$ , and  $\text{TlNO}_3$  are given in Table 1. Apart from the  $\text{TlNO}_3$ -III-II transition, involving a relatively small

*Table 1.* Polymorphism in nitrates.<sup>1</sup> Numbers in parentheses are temperatures in degrees centigrade, and indicate stability regions at atmospheric pressure. \* Isostructural compounds. \*\* Isostructural compounds.

Crystal form	$\text{RbNO}_3$	$\text{TlNO}_3$	$\text{CsNO}_3$
Rhombic "Pseudo-hexagonal"	IV (< 164) *	III (< 75) II (75-143) *	II (< 154) *
Cubic	III (164-220)**	I (> 143)**	I (> 154)**
Rhombohedral	II (220-291)		
Cubic	I (> 291)		

entropy change, the transformations are probably associated with changes in orientational order of the system.<sup>1</sup>

The structures of the high-temperature forms of these compounds are the subject of the present study, which is largely based on comparing experimental entropy data with values of orientational entropy evaluated in a similar manner as done recently for  $\text{NaNO}_3$ -I<sup>2</sup> and  $\text{KNO}_2$ -I<sub>2</sub>.<sup>3</sup>

THE STRUCTURE OF  $\text{RbNO}_3$ -III,  $\text{CsNO}_3$ -I, AND  $\text{TLNO}_3$ -I

Since these crystal phases are isostructural, the discussion will mainly be concerned with the structure of  $\text{RbNO}_3$ -III. Finbak and Hassel<sup>4</sup> reported  $\text{RbNO}_3$ -III and  $\text{CsNO}_3$ -I to be cubic primitive, the unit cell containing one molecule of metal nitrate. The nitrate groups were thought to rotate spherically about the mass centre.<sup>4</sup> More recently Korhonen<sup>5,6</sup> assumed that the space group is the centro-symmetric  $Pa\bar{3}$ , with eight molecules in the unit cell. He obtained a satisfactory agreement between experimental and calculated structure factors on the basis of an orientationally ordered structure, involving aragonite-type orientations of the nitrate group connected to three nearest metal ions through a single O-Rb contact per oxygen atom.

There are, however, several reasons for modifying this model to incorporate orientational randomness of the nitrate ions:

(a) The relatively high value of the entropy change observed in the IV-III transition in  $\text{RbNO}_3$  (and similarly for the two other compounds) indicates phase III to be disordered.<sup>1</sup>

(b) The configurational entropy of form II is greater than the value observed in the III-II transition, which may be explained as due to orientational disorder in phase III.

(c) The ordered model incorporates two sets of metal ions (in  $(0,0,0)$ , etc., and in  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  etc., using the notation of Korhonen<sup>5,6</sup>), one involving a normal contact distance between the metal ions and the oxygen atoms, 2.93 Å, whereas the second set gives rise to metal-oxygen separations not smaller than 3.22 Å, which seems improbable.

(d) Only reflections with even values of the indices are incorporated in the calculation of the  $R$ -value.<sup>5</sup> These are the only type of reflection to which the metal ions contribute. However, for some of the reflections for which  $h+k+l=2n+1$ , the values of structure factors computed from the ordered structure are quite high, whereas these reflections actually are apparently nonobservable.<sup>5</sup> For these reflections the agreement between observed and calculated structure factors is not quite satisfactory. However, some reflections of this type were observed after elongated exposure. This will be considered below but ignored at present.

The alternative space group  $Ia\bar{3}$ , yielding the same values of the structure factors of even indices, cannot give rise to orientational disorder because of a short O-O separation of 1.77 Å occurring between "disordered" orientations of neighbouring nitrate groups. A similar conclusion applies even if calcite-type orientations are incorporated.

The X-ray data are in accordance with a cubic configuration of the metal ions as in the ordered model, wherein the metal ions are placed at the eight corners of a cube (and a single nitrate group at the centre). In an isolated cube there are, however, eight equivalent aragonite-type orientations of the nitrate ion, the three-fold axis of which coincides with either of the four three-fold axes of the cube. Likewise, there will in principle be eight calcite-type orientations obtained by rotating the nitrate group 30° around the three-fold axes from aragonite-type positions etc., so that each oxygen becomes equally distant from two neighbour metal ions.

In the lattice, many of these orientations are blocked at a given moment, due to interactions between neighbouring nitrate groups, even if the *instantaneous* orientations may deviate somewhat from those defined above. Inspection shows, however, that a disordered state is obtained in such a system.

This model of the structure corresponds to a statistical unit cell containing one molecule, in agreement with the original proposal.<sup>4</sup> The symmetry corresponds to the space group  $Pm\bar{3}m$  (which is equivalent to  $Pm\bar{3}$  for the special positions in question). In agreement with the notation in the *International Tables*, the nitrate groups are centred about the origin, *etc.*, whereas the rubidium ions occupy positions  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , *etc.* For the reflections in question, the  $R$ -value based on this model is exactly the same as before, the ordered model<sup>5,6</sup> being contained in the present one. However, introduction of some calcite-type character into the structure improved the  $R$ -value somewhat. The best agreement was obtained at 18 % calcite-type character, which gave an  $R$ -value of 7.8 % in a simple calculation as compared to 8.3 % for the pure aragonite-type structure using Korhonen's experimental data. Since the corresponding metal-oxygen distance is of reasonable magnitude (Table 2), a certain amount of calcite-type character in the structure appears likely.

Table 2. Intermolecular (statistical) distances in  $\text{RbNO}_3$ -III. The NO-distance is assumed equal to 1.25 Å,  $a = 4.37$  Å. Basic positional parameters are as follows for aragonite-type positions: N( $x, x, x$ ):  $x = 0.070$  (equivalent to the value published previously<sup>6</sup>), and O( $x, x, z$ ):  $x = -0.047$ ,  $z = 0.304$ . For calcite-type positions: N(0,0,0) and O(0, $\bar{z}, z$ ):  $z = 0.202$ , the 3-fold axis of the nitrate group coinciding with the (111)-direction of the unit cell. The rubidium ions are situated in  $(\pm \frac{1}{2}, \pm \frac{1}{2}, \pm \frac{1}{2})$ .

Distance	Length (Å)	Distance	Length (Å)
N(0,0,0) - Rb( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ )	3.79	A - C	
N( $x, x, x$ ) - Rb( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ )	3.26	O( $x, x, z$ ) - O(0, $z, 1-z$ )	2.27
O( $x, x, z$ ) - Rb( $-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}$ )	2.93	O( $x, x, z$ ) - O(1, $z, 1-z$ )	2.43
O( $x, x, z$ ) - Rb( $\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}$ )	3.22	C - A	
O(0, $\bar{z}, z$ ) - Rb( $-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}$ )	2.86	O(0, $\bar{z}, z$ ) - O( $x, x, 1-z$ )	2.27
O(0, $\bar{z}, z$ ) - Rb( $\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}$ )	2.86	O(0, $z, z$ ) - O( $\bar{x}, x, 1-z$ )	2.27
A - A		O(0, $\bar{z}, z$ ) - O( $x, -1+z, \bar{x}$ )	2.27
O( $x, x, z$ ) - O( $x, x, 1-z$ )	1.72	O(0, $\bar{z}, z$ ) - O( $\bar{x}, -1+z, \bar{x}$ )	2.27
O( $x, x, z$ ) - O( $x, \bar{x}, 1-z$ )	1.77	O(0, $\bar{z}, z$ ) - O( $x, \bar{x}, 1-z$ )	2.43
O( $x, x, z$ ) - O( $\bar{x}, x, 1-z$ )	1.77	O(0, $\bar{z}, z$ ) - O( $\bar{x}, \bar{x}, 1-z$ )	2.43
O( $x, x, z$ ) - O( $\bar{x}, \bar{x}, 1-z$ )	1.81	O(0, $\bar{z}, z$ ) - O( $x, -1+z, x$ )	2.43
		O(0, $\bar{z}, z$ ) - O( $\bar{x}, -1+z, x$ )	2.43
		C - C	
		O(0, $\bar{z}, z$ ) - O(0, $\bar{z}, 1-z$ )	2.60
		O(0, $\bar{z}, z$ ) - O(0, $-1+z, z$ )	2.60

Values of intermolecular distances are listed in Table 2. Only O - O separations less than 2.8 Å are incorporated. These were assumed to be too short to actually occur at equilibrium and therefore excluded in the subsequent estimation of the orientational (configurational) entropy based on the present model. The Rb - O (calcite) contact separation is seen to be somewhat shorter than the Rb - O (aragonite) distance, the mean value of these distances being

close to the sum of the ionic radii, 2.89 Å.<sup>1</sup> The N–Rb separations are all well above the sum of the van der Waals radius of nitrogen and the ionic radius of rubidium.

A value of the configurational entropy of the system was worked out on the basis of this model. For simplicity, only interactions between a chosen central nitrate group and the six nearest neighbours were considered explicitly in the calculation, *i.e.* the microsystem contains effectively two nitrate groups.

The configurational entropy,  $\Delta S(\text{conf.})$ , is then given by the following relationship:<sup>2</sup>

$$\Delta S(\text{conf.}) = R(x_A \ln g_A/x_A + x_C \ln g_C/x_C) + R/2 \ln(1-s)$$

where  $s$  in the present case takes the form

$$s = g_A \{ (n_{A_2} s_A^2 + n_{AC} s_A s_C) - (n_{A_3} s_A^3 + n_{A_2 C} s_A^2 s_C + n_{AC_2} s_A s_C^2) \text{ etc.} \} \\ + g_C \{ (n_{C_2} s_C^2 + n_{CA} s_C s_A) - (n_{C_3} s_C^3 + n_{C_2 A} s_C^2 s_A + n_{CA_2} s_C s_A^2) \text{ etc.} \}$$

where  $s_A = x_A/g_A$  *etc.*, and  $x_A$  is the fraction of molecules occupying aragonite-type positions, the statistical number of which is denoted by  $g_A$ .  $n_{CA}$  is the number of forbidden A-type orientations of nitrate groups, relative to a given C-type position, whereas  $n_{AC_2}$ , for instance, is the number of forbidden C-type orientations of two and two neighbouring nitrate groups, relative to a given A-type position.

*Table 3.* The distribution of the number of instantaneously forbidden orientations of nitrate groups, L, relative to a given (either aragonite- or calcite-type) orientation of the nitrate group at the origin, S (3//[111]), according to space group  $Pm\bar{3}m$ , using the results of Table 1.

	L	L	L	L	L	L
S–L	(1,0,0)	(0,1,0)	(0,0,1)	( $\bar{1}$ ,0,0)	(0, $\bar{1}$ ,0)	(0,0, $\bar{1}$ )
A–A	4	4	4	0	0	0
A–C	8	8	8	0	0	0
C–A	4	4	4	4	4	4
C–C	2	2	2	2	2	2

Using  $x_A = 0.82$ ,  $g_A = g_B = 8$ , and the result of Table 3, one obtains  $\Delta S(\text{conf.}) = (5.07 - 2.78)$  cal/mol K = 2.29 cal/mol K in good agreement with the observed entropy change of the IV–III transition, 2.15 cal/mol K, obtained after deducting the specific heat contribution from the total energy input in the transformation.<sup>1</sup> (In comparison a pure aragonite-type structure leads to  $\Delta S(\text{conf.}) = 2.07$  cal/mol K.)

However, apart from the uncertainty inherent in the evaluation of the orientational entropy, *etc.*, one may in general expect the  $\Delta S(\text{conf.})$ -value rather to be somewhat less than the transition entropy. The present model may therefore overestimate to some extent the actual orientational entropy of RbNO<sub>3</sub>–III.

There are some observations in accordance with this. Firstly, Korhonen<sup>5</sup> was able to record faint intensities of intermediate reflections after elongated exposure, corresponding to a statistical unit cell, containing eight molecules.

In the present scheme, this result may be interpreted as an effect of molecular correlation, reducing the randomness somewhat and therefore also the orientational entropy implied by the proposed model. Or, in other words, the energy of the system is too small to maintain such a high degree of randomness. Although expected to be relatively small, the corresponding change in entropy or structure from the results obtained above is difficult to ascertain.

Secondly, the statistical symmetry group of the nitrate ion is accordingly not  $m3m$ , corresponding to space group  $Pm3m$ , but rather a less symmetric one. This seems reasonable, compared with the point group symmetry,  $\bar{3}m$ , of the nitrate group in the rhombohedral phase II, since the statistical symmetry of an orientationally disordered system is likely to increase with increasing temperature, in view of the second law of thermodynamics, and not to decrease.

#### THE STRUCTURE OF $RbNO_3$ -II

$RbNO_3$ -III transforms into the rhombohedral variety  $RbNO_3$ -II at about 220°C.<sup>7</sup> The latter phase resembles the high-temperature forms of sodium and potassium nitrate.<sup>4,7</sup> It seems therefore natural to assume at first the nitrate groups to occupy the same types of orientation as recently proposed for  $NaNO_3$ -I<sup>2</sup> and  $KNO_3$ -I<sup>3</sup> (*i.e.* calcite- and aragonite-type positions of the nitrate groups, whose three-fold symmetry axes coincide with the hexagonal *c*-axis). The space group is accordingly  $R\bar{3}m$ . Interatomic distances were calculated on this basis, using the unit cell dimensions given by Finbak *et al.*<sup>7</sup> An approximate value of the *z*-parameter of the nitrate group in the aragonite-type position was obtained by assuming the Rb-O (aragonite) separation equal to the Rb-O (calcite) distance, obtained as 2.81 Å. This number is somewhat smaller than obtained for phase III, which is surprising. The N-Rb separations are all well above the sum of the van der Waals radius of nitrogen and the ionic radius of rubidium.

It appears that all O-O separations in this model are longer than 2.8 Å. The *s*-term in the  $\Delta S$  (conf.)-equation is thus equal to zero. However, the population ratio of the two sets of orientation is not known. A 1:1 distribution corresponds to a maximum value of 2.75 cal/mol K for the orientational entropy, whereas an unsymmetric distribution of say, 1:10, leads to 2.03 cal/mol K. These figures are significantly greater than the experimental III-II entropy change of 1.55 cal/mol K, supporting the previous conclusions.

However, according to calculations outlined below, the orientational entropy of  $RbNO_3$ -I is considerably higher than the sum of the maximum value, 2.75 cal/mol K, implied by the present model, and the observed entropy change of the II-I transition, 0.42 cal/mol K.<sup>1</sup> The discrepancy may be explained in terms of an extended orientational nitrate group disorder in  $RbNO_3$ -II, relative to that implied by the present model.

Consideration of intermolecular Rb-O and Rb-N distances indicates that a nitrate group may be placed at a normal Rb-O contact with the three Rb-ions in (1/3, -1/3, 1/6), (2/3, 1/3, -1/6), and (1/3, 2/3, 1/6) (not related by simple three-fold symmetry) without producing unacceptable intermolecular distances of these types. However, some of the orientations may be blocked at a given moment because of intermolecular O-O interactions.

In this indicated type of position, the nitrogen and an oxygen atom occupy positions at the mirror plane, containing  $(2/3, 1/3, -1/6)$  and the  $z$ -axis, whereas the other two O-atoms are situated on either side of the mirror plane. It appears that two sets of such positions may be thought of as equilibrium orientations, each incorporating six statistically equivalent orientations of the nitrate group. The first type of position involves one Rb-O contact distance per oxygen atom, the second, which may seem less likely, since some of the metal nitrogen separations are somewhat short (2.98 Å for the chosen position, involving O-O separations of about 2.91 Å) relative to general observations, involves two Rb-O contact distances for each of two oxygens and one contact for the third. However, only approximate positions can be deduced in this way.

On transforming to RbNO<sub>3</sub>-I, these two sets of position become, along with the two proposed previously, two sets of respectively eight equivalent aragonite-type positions and eight equivalent calcite-type positions, each of which having a threefold symmetry axis common with those of the space group. A rough calculation indicates that about 25 % or more of the nitrate groups may be needed in the suggested, additional types of position, to obtain a configurational entropy, corresponding to about 5 cal/mol K suggested for RbNO<sub>3</sub>-I. In the rhombohedral forms I of KNO<sub>3</sub> and NaNO<sub>3</sub> this fraction is evidently considerably smaller.

A structure based on an extended disorder as discussed above seems more plausible as an intermediate between phases I and III, than is the original model, wherein all threefold axes of the nitrate groups are aligned in the same direction.

It has been suggested that RbNO<sub>3</sub>-II may alternatively be indexed as tetragonal.<sup>8</sup> The threefold axis of the statistical point group symmetry of the nitrate ion referring to phase III would thereby be lost in the III-II transformation. Such a situation seems unlikely from a thermodynamic viewpoint. A similar conclusion is also made by Newns and Stavely<sup>1</sup> on a different basis.

#### THE STRUCTURE OF RbNO<sub>3</sub>-I

RbNO<sub>3</sub>-II changes into the cubic, face-centred form RbNO<sub>3</sub>-I at about 291°C.<sup>1,8</sup> The points  $(1,0,0)$ ,  $(0,1,0)$ ,  $(0,0,1)$ , etc., in the unit cell of RbNO<sub>3</sub>-III indexed as primitive (equal to the rhombohedral cell, containing one molecule in rhombohedral indexing) transform into  $(\frac{1}{2}, \frac{1}{2}, 0)$ ,  $(0, \frac{1}{2}, \frac{1}{2})$ ,  $(\frac{1}{2}, 0, \frac{1}{2})$ , etc., of the face-centred unit cell of RbNO<sub>3</sub>-I, respectively, on going from III via II to I. Similarly, the anion positions  $(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$ ,  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ,  $(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$ , etc., become the points  $(\frac{1}{2}, 0, 0)$ ,  $(0, \frac{1}{2}, 0)$ ,  $(0, 0, \frac{1}{2})$ , etc., respectively. A marked elongation of the hexagonal  $c$ -axis (in the cubic [111]-direction) takes place, whereas a contraction in perpendicular directions occurs in both transitions. The molecular volume increases, however, as shown in the following sequence:  $v(\text{IV}) = 77.55 \text{ \AA}^3$ ,  $v(\text{III}) = 83.45 \text{ \AA}^3$ ,  $v(\text{II}) = 92.88 \text{ \AA}^3$ , and  $v(\text{I}) = 98.06 \text{ \AA}^3$ .

The structure of RbNO<sub>3</sub>-I is of the NaCl-type.<sup>1</sup> Accordingly, the nitrate group centred about  $(0,0,0)$  is surrounded by six nearest Rb-ions in  $(\frac{1}{2}, 0, 0)$ , etc., in an octahedral configuration. In accordance with the models obtained for the other phases, the nitrate groups are expected to occupy statistically

aragonite- and calcite-type orientations, of which there are eight of each kind per nitrate group, as pointed out by Newns and Stavely.<sup>1</sup> The statistical point group symmetry of the anion is  $m\bar{3}m$  and the space group  $Fm\bar{3}m$ , as the randomization according to this model is expected to be complete in the high-energetic phase in question.

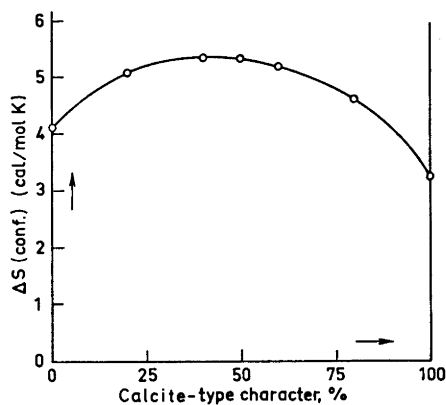
Values of intermolecular distances are contained in Table 4 along with positional parameters, *etc.* The Rb–O (calcite) separation is about 0.1 Å

*Table 4.* Interatomic distances in  $\text{RbNO}_3$ –I. The N–O separation was assumed equal to 1.25 Å;  $a = 7.32$  Å.<sup>8</sup> Aragonite-type position: N( $x,x,x$ ):  $x = -0.0007$ , and O( $x,x,z$ ):  $x = -0.087$ ,  $z = 0.122$ . Calcite-type position: N( $0,0,0$ ) and O( $0,\bar{z},z$ ):  $z = 0.121$ . The metal ions are situated in  $(0,0,\frac{1}{2})$ , *etc.* All O–O separations are greater than 2.9 Å, except the listed one, which is considerably smaller than the normal contact distance of 2.8 Å. Inspection shows that the position of the nitrate group centred about the origin with oxygen coordinates  $(0,\bar{z},z)$ ,  $(z,0,\bar{z})$ , and  $(\bar{z},z,0)$  gives rise to two unacceptable positions of the nitrate group at  $(0,-\frac{1}{2},\frac{1}{2})$ ,  $(\frac{1}{2},0,-\frac{1}{2})$  and  $(-\frac{1}{2},\frac{1}{2},0)$ , respectively.

Distance	Length (Å)
N( $0,0,0$ )–Rb( $0,0,\frac{1}{2}$ )	3.66
N( $x,x,x$ )–Rb( $0,0,-\frac{1}{2}$ )	3.61
O( $0,\bar{z},z$ )–Rb( $0,0,\frac{1}{2}$ )	2.91
O( $0,\bar{z},z$ )–Rb( $0,-\frac{1}{2},0$ )	2.91
O( $x,x,z$ )–Rb( $0,0,\frac{1}{2}$ )	2.91 (ass.)
O( $x,x,z$ )–Rb( $0,-\frac{1}{2},0$ )	3.21
O( $0,\bar{z},z$ )–O( $0,-\frac{1}{2}+z,\frac{1}{2}-z$ )	2.68

larger than this distance referred to phase II, or close to the sum of the ionic radii. The Rb–O (aragonite) distance was assumed equal to the present one in the determination of the aragonite-type position of the nitrate group.

Values of the orientational entropy, shown plotted against calcite-type character in Fig. 1, were calculated in the same way as described for phase III, obtaining the necessary information from Table 4. For thermodynamic reasons the calcite-type character would be expected to increase with temperature and thus possibly be somewhat higher than in  $\text{RbNO}_3$ –III, and therefore



*Fig. 1.* Computed configurational entropy of  $\text{RbNO}_3$ –I, shown plotted against per cent calcite-type character.

closer to the value yielding maximum configurational entropy (Fig. 1), *i.e.* of the order of 5 cal/mol K.

### CATION DISORDER

The observed transition entropies of the metal nitrates studied so far have been interpreted reasonably satisfactorily without considering cation positional disorder, although there is room for a small contribution of this origin in most cases. However, an appreciable cation positional disorder may in principle exist without affecting significantly the entropy. A more definite statement of the number of accessible equilibrium positions of a cation in a given configuration of the neighbouring ions would require knowledge of the proper potential functions, representing the interaction between the cation and the surrounding ions. In practice, several somewhat arbitrary assumptions will have to be made, rendering the results correspondingly more uncertain.

### THE BASIC MODEL OF DISORDER

The structures of the metal nitrates discussed here and elsewhere<sup>2,3</sup> represent the Frenkel model of disorder,<sup>9,10</sup> according to which each molecule may take only certain orientations. Molecular reorientation between equilibrium positions occurs normally at a considerably lower rate than the librational frequency in the potential wells. The Frenkel model has generally been found to be in accordance with experimental<sup>1,3,9</sup> and theoretical evidence<sup>11</sup> in related cases, contrary to the free (or hindered) rotational model.<sup>9,11</sup>

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