Interpretation of the Solution Absorption Spectra of the $(PuO_2)^{++}$ and $(NpO_2)^+$ Ions

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Eleven years ago we proposed a model for the electronic configuration of ions of the uranyl type. The solution absorption spectra of the $(PuO_2)^{++}$ and $(NpO_2)^+$ ions are here interpreted on the basis of this model. The interpretation is based on exact calculations, and on plausible arguments about the strengths and widths of the absorption peaks. If suitable values are chosen for the Coulomb integrals, the spin-orbit coupling constant, and the ligand field parameters then the calculated energy levels agree well with the observed positions of the absorption peaks.

Key Words: $(NpO_2)^+$ ion, plutonyl ion, absorption spectrum.

1. Introduction

Eleven years ago we published a paper [1][1] on the magnetic and spectroscopic properties of the plutonyl ion. We now know [2] that the parameters which we used in calculating the energy levels were assigned the wrong values. Despite this unhappy circumstance the correct interpretation was given to the dominant peaks in the absorption spectrum and, since the ground state of the ion was correctly identified, the calculated magnetic properties agreed with the meager available experimental data.

Our purpose in this paper is partly to present revised values of the parameters and new calculations of the energy levels. Our primary purpose is to discuss in detail the absorption spectra of the isoelectronic $(PuO_2)^{++}$ and $(NpO_2)^+$ ions, both of which have two electrons outside what we might call the uranyl core. We have been curious to see the extent to which plausible, semiquantitative arguments about strengths and widths of absorption lines could be used in identifying the rather complex solution absorption spectra of these ions.

In analyzing the $(NpO_2)^+$ and $(PuO_2)^{++}$ spectra the first important question which one has to decide is whether the ligand field strengths for these ions are the same as those for the neptunyl ion. Information bearing indirectly on this point comes from the infrared measurements of Jones and Penneman [3] on uranyl and transuranium (V) and (VI) ions in aqueous solu-

tions. Table 1 gives the asymmetric stretching frequencies of these ions as determined by Jones and Penneman. The similarity of the stretching frequencies for the first four ions in the table indicates that the ligand fields are similar for all four. On the other hand, since for $(NpO_2)^+$ and $(AmO_2)^+$ the vibration energies are lower, the bond length is probably greater and the ligand field weaker.

TABLE 1. *Asymmetric stretching frequencies of uranyl-type ions in aqueous perchloric acid solution*

Ion	Frequency/c
	cm^{-1}
$(UO_2)^{++}$	965
$(NpO_2)^{++}$	969
$(PuO_2)^{++}$	962
$(AmO_2)^{++}$	939
$(NpO_2)^+$	824
$(AmO_2)^+$	832

Indirect information on the variation of the ligand field strengths in the uranyl type ions can also be obtained by studying the variation of the crystal field parameters in any series of structurally similar compounds. For example, for several rare earth trichlorides [4] the variation from one rare earth ion to the next is probably 10 or 20 percent.

Data on the absorption spectrum of the $(UO_2)^+$ ion would yield important information on the strength of the ligand field in $(NpO_2)^+$ if it is really the case that

similar ions have similar fields. The only experiments on the $(UO_2)^+$ absorption have been done by Kraus, Nelson, and Johnson [5]. They found no absorption peak with a molar extinction coefficient as high as 1.5 in the region between 10,000 and 27,800 cm^{-1}. The peaks corresponding to the transitions to $|1->$ and $|1+>$ should fall in this region. In neptunyl they have extinction coefficients of approximately 6. The more intense absorption peaks, which the $(UO_2)^+$ spectrum should have, occur below 10,000 cm^{-1}.

To begin the calculations we assumed that the ligand field strengths were the same for $(PuO_2)^{++}$ as for $(NpO_2)^{++}$ and were about 15 percent smaller for $(NpO_2)^+$. This assumption proved to be a reasonable starting point.

One expects the value of ζ to be larger for the plutonyl ion than for the neptunyl ion because the spin-orbit coupling constant generally increases with increasing atomic number. ζ may not have quite the same value for $(NpO_2)^+$ as for $(NpO_2)^{++}$ because the overlap of the wave functions on the surrounding ions may be slightly different.

The important additional complication in the two-electron spectra is the Coulomb repulsion of the electrons. The calculation of the matrix elements is considerably facilitated by use of table 1 of Condon and Shortley's [6] book. All the matrix elements of the Coulomb interaction depend on numerical factors, which can be obtained from the table, and on the four radial integrals $F^{(0)}$, $F^{(2)}$, $F^{(4)}$, and $F^{(6)}$ or, more conveniently, the parameters $F_0 = F^{(0)}$, $F_2 = F^{(2)}/225$, $F_4 = F^{(4)}/1089$ and $F_6 = 25 \ F^{(6)}/(429)^2$. In practice, we have followed Racah by using the linear combinations:

$$L = 5F_2 + 6F_4 - 91 \ F_6$$

$$A = 924 \ F_6$$

$$B = 14 \ F_4 - 84 \ F_6.$$

We used a Fermi-Thomas model to calculate a $5f$ radial wave function appropriate to Pu^{5+} from which Basu calculated $F^{(2)} = 79,000$ cm^{-1}. We then used an approximate wave function to calculate the relative values of the $F^{(2n)}$. We found, for example, that $L = 1577$ cm^{-1}. A further useful guide comes from the wave functions calculated by Ridley [7] for U^{6+} by a Hartree method. For the $5f$ electrons she found $F_0 = 137,340$ cm^{-1}, $F_2 = 297.9$ cm^{-1}, $F_4 = 39.68$ cm^{-1} and $F_6 = 4.281$ cm^{-1}; therefore $L = 1338$ cm^{-1}. These calculations give one only a rough idea of the values of L, A, and B. The actual values of these parameters in $(PuO_2)^{++}$ and $(NpO_2)^+$ must be determined by analyzing the absorption spectra.

2. Procedure

In our analysis of the $(NpO_2)^{++}$ data in III we had ten parameters at our disposal when covalent effects and

ligand fields of threefold and sixfold symmetry were considered. For $(NpO_2)^+$ and $(PuO_2)^{++}$ six additional parameters are required to characterize the Coulomb interaction (covalent effects included). The total of 16 parameters is inconveniently large. We have therefore simplified the problem by leaving out of consideration covalent effects and ligand fields with three-fold symmetry. We hoped that by varying the eight remaining parameters we would be able to obtain agreement with at least the gross features of the observed spectra, and this hope has been fulfilled. It is not difficult to include the neglected effects in the calculations, and this should probably be done when low-temperature absorption spectra of crystalline uranyl-type compounds become available.

In II we excluded from consideration the σ-states — i.e., states in which m_l for one or both electrons is zero. However, we have included these states here. When the Coulomb and the spin-orbit interactions are taken into account, and the ligand fields of axial and sixfold symmetry, one obtains secular equations of order 12, 5, 14, 16, 7, and 7. These numbers correspond, respectively, to crystal field quantum numbers 0, 0, 1, 2, 3, and 3. The secular equations can readily be solved, for particular values of the parameters, by using an electronic computer.

Our procedure in analyzing each spectrum was to select values for all the eight parameters and then to calculate eigenvalues and eigenvectors. The calculated eigenvalues were studied in relation to the known absorption spectrum and an attempt was made to find improved values of the parameters. These improved values were then used for another calculation of the energy levels. The procedure was repeated until we had what we felt was the most satisfactory possible interpretation of the spectrum.

3. The Plutonyl Spectrum

For both the $(NpO_2)^+$ and the $(PuO_2)^{++}$ ions the principal component of the ground state is the $^3H_4$ $|3-, 2->$ state [8, 9]. In the absence of the "crystalline" field Hund's rules place this state lowest. In all the calculations we have done, with widely varying values of the parameters, $^3H_4$ has been found to be lowest. Finally, and most important, the paramagnetic resonance data on crystalline plutonyl rubidium nitrate [10] and plutonyl sodium acetate [11] indicate unambiguously that the ground state is $^3H_4$. Therefore in discussing the absorption spectra we shall assume, without further comment, that all transitions take place from a ground state which is predominantly $^3H_4$.

The absorption spectra of the $(PuO_2)^{++}$ and $(NpO_2)^+$ ions are shown in figures 1 and 2. It will be seen that the two spectra have certain similarities particularly in their low frequency regions. The spectrum of $(PuO_2)^{++}$ is shifted towards higher frequencies relative to that of $(NpO_2)^+$.

The most prominent peak in the plutonyl spectrum is the one at 12,037 cm^{-1} for which the molar extinction

coefficient is 300, the width at half maximum is 34 cm^{-1} and the strength [12] is about 31. We regard the identification of this peak as predominantly $^3\Pi_2$ $|2-, -3->$ as certain. The transition which takes place is $|3-, 2->\rightarrow|-3-, 2->$. We have already argued in III that the $3\rightarrow-3$ transitions should give rise to narrow absorption peaks. The fact that they are strong as well was of crucial importance in the interpretation of the neptunyl spectrum. By suitably choosing the values of the Coulomb integrals and the spin-orbit coupling constant other levels, rather than the $|2-, -3->$ level, can be made to fall at 12,037 cm^{-1}. However, if such a choice is made one is left without a plausible identification for the next most prominent peaks at 10,185 and 10,500 cm^{-1}.
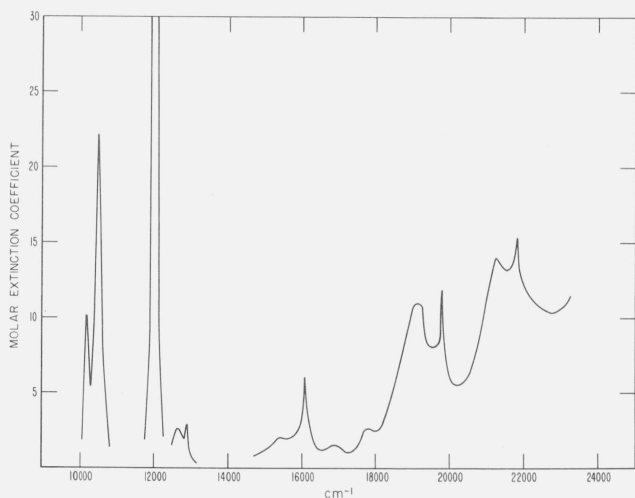
We identify these peaks, in part, as due to the transitions $2\rightarrow-2$ to a split $^3\Pi_0$ level. The apparent degeneracy of the states $|3-, -2->$ and $|2+, -3+>$ is removed by the spin-orbit coupling in a second order perturbation calculation [13]. The symmetric combinations

$$|3-, -2->+|2+, -3+>$$

etc., are coupled by $\zeta\, \mathbf{L}\cdot\mathbf{S}$ to the Σ_0 states. The antisymmetric combinations, however, are not coupled to any other states by $\zeta\, \mathbf{L}\cdot\mathbf{S}$. They are coupled to one another by the Coulomb interaction, and to $^1I_6$ by the ligand field component which has sixfold symmetry. We shall refer to these antisymmetric combinations as $^3\Pi_0'$ states, and to the symmetric combinations as $^3\Pi_0$ states although this notation is the reverse of that used in our previous paper on the plutonyl ion (II). One finds, as a result of calculation, that the $^3\Pi_0'$ $|3-, -2->$ state lies below the corresponding $^3\Pi_0$ state. Since $^3\Pi_0'$ $|3-, -2->$ interacts weakly with the other $^3\Pi_0'$ states, and since it can be reached from the $^3H_4$ ground state by a $2\rightarrow-2$ transition which leaves the charge distribution nearly unaffected, we conclude that the $^3\Pi_0'$ peak should be narrow. If we adjust the parameters of our theory so that $^3\Pi_2$ is located near 12,000 cm^{-1} then we find that $^3\Pi_0'$ lies near 10,000 cm^{-1}. Its position is rather insensitive to all parameters except ζ and $\mathbf{L}$. We therefore identify the peak at 10,185 cm^{-1} as due to transitions to $^3\Pi_0'$, and we regard this identification as virtually certain.

The experimental peak at 10,500 cm^{-1} probably consists of two unresolved peaks since the absorption curve has a well developed shoulder [14] at about 10,700 cm^{-1}. One of these unresolved peaks is due to transitions to $^3\Pi_0$ $|3-, -2->$. The peak should be wider and also less intense than the $^3\Pi_0'$ peak because of the extensive coupling of $^3\Pi_0$ to other states.

FIGURE 2. *Absorption spectrum of* Np (V) *in 1.0* M DClO$_4$–D$_2$O.
The curve has been replotted from data given by W. C. Waggener in J. Phys. Chem. **62**, 382 (1958).
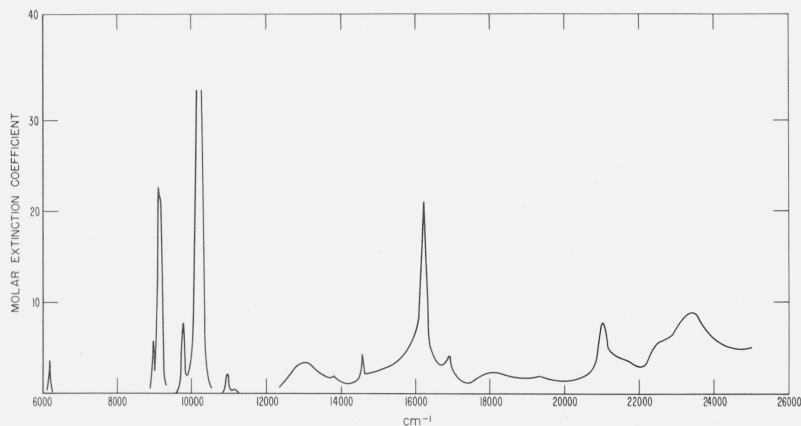

FIGURE 1. *Absorption spectrum of* Pu (VI) *in 0.5* M HCl.
The curve has been replotted from data given by R. E. Connick, M. Kasha, W. H. McVey and G. E. Sheline in The Transuranium Elements, National Nuclear Energy Series, IV, 14b, McGraw-Hill Book Co., New York, 1949. (Paper 4.20, figs. 12–15.)

The calculations place $^3\Pi_0$ in the vicinity of 10,700 cm^{-1}, and since the shoulder has less strength than the peak we have identified with $^3\Pi_0'$, we ascribe the unresolved 10,700 cm^{-1} peak to $^3\Pi_0$.

The other component of the unresolved doublet is probably a Σ_1 state. The transitions that give rise to this absorption peak are $|3-, \ 2->\rightarrow|-2-, \ 2->$ and $|3-, \ 2->\rightarrow|3-, \ -3->$; that is, they are $3\rightarrow-2$ and $2\rightarrow-3$ transitions. For the neptunyl ion the $3\rightarrow-2$ transitions are almost as narrow as the $3\rightarrow-3$ transitions, so one can expect the same to be true for the plutonyl ion. They are, however, less probable [15]. It therefore seems likely that the experimental peak at 10,500 cm^{-1} should be identified with transitions to Σ_1. The principal difficulty with this assignment is that the peak has at least twice the strength we would expect from our study of the neptunyl spectrum. We regard the identification of the unresolved structure between 10,300 and 10,800 cm^{-1} as partly Σ_1 and partly $^3\Pi_0$ as pretty certain, but it is difficult to say precisely where the two peaks should lie.

The two small peaks at 12,660 and 12,890 cm^{-1} may be due either to the $^3H_6$ and $^3H_6'$ states or to the vibrational fine structure of the 12,037 cm^{-1} peak. The charge distribution in the $^3H_6$ states is such that the corresponding absorption peaks should be narrow. They should also be weak since the absorption is due principally to the contamination of the $^3H_6$ states by $^3\Pi_0$ states. We consider it unlikely that the two peaks are due to transitions to the $^3H_6$ and $^3H_6'$ states because the separation of these states is less than 100 cm^{-1} in almost all of our calculations.

If the peaks are to be ascribed to vibrations the vibrational energy would have to be 620 or 850 cm^{-1}. The energies of the symmetric and antisymmetric stretching vibrations in the ground state of solid sodium plutonyl acetate are 818 and 930 cm^{-1} respectively [16]. Therefore we consider it reasonable to assign the peak at 12,890 cm^{-1} to the symmetric stretching vibration. Since the charge distribution in the excited $^3\Pi_2$ state is nearly the same as in the ground state the vibrational energies should be nearly the same in the excited state as in the ground state. Despite the fact that the $3\rightarrow-3$ transitions do not excite many vibrations the peak at 12,890 cm^{-1} shows up because of the very great strength of the 12,037 cm^{-1} peak.

The $^3H_6$ doublet is probably not resolved, both components being concealed in the single hump at 12,660 cm^{-1}. One can perhaps understand in this way why the 12,660 cm^{-1} peak is broader than one would expect for $^3H_6$.

There now follows a discussion of the identification of the remaining peaks of the experimental absorption spectrum of the plutonyl ion. These identifications rest on arguments about intensities and breadths and on detailed calculations of the positions of the energy levels. In contrast to the peaks just discussed we do not regard the identification of any of the remaining peaks as certain. The difficulty we have encountered can be stated in the following way. Depending on the choice of parameters either there are too few calculated levels in the region from 15,000 to 25,000 cm^{-1}, or else there are calculated levels with no corresponding observed levels.

This circumstance makes it necessary for us to concentrate our attention on what we think are the principal transitions, and on the dominant features of the experimental spectrum. Consider the possible "allowed" transitions from the $^3H_4$ $|3-, \ 2->$ ground state. They are $3\rightarrow-3, \ -2, \ -1, \ 0$, or 1 and 2 $\rightarrow-3, \ -2, \ -1, \ 0$, or 1. We have already located the $3\rightarrow-3$ and the $2\rightarrow-2$ transitions. The $3\rightarrow0$ and $2\rightarrow0$ transitions are almost certainly well above 25,000 cm^{-1} since an electron in an $m_l=0$ state is strongly repelled by the axial charge distribution. Due to the extensive mixing of the Π_1 and Σ_1 states it is unlikely that the $3\rightarrow-2$ and $2\rightarrow-3$ transitions will give rise to any peaks that are stronger than the peak at 10,500 cm^{-1} which we have associated with a Σ_1 state. The remaining possible transitions are $3\rightarrow-1$ or 1 and $2\rightarrow-1$ or 1. The calculations place the excited states in the following order of ascending energy: $^3\Gamma_3$ and $^3\Gamma_3'$ $(2\rightarrow1)$ [17], $^3\Phi_2$ $(3\rightarrow1)$, $^3\Delta_1$ $(2\rightarrow-1)$, $^3\Pi_0'$ and $^3\Pi_0$ $(3\rightarrow-1)$.

For the neptunyl ion the $3\rightarrow2$ transition is relatively narrow, probably because the change in the charge distribution is mainly in the equatorial region and does not excite vibrations of the ion, or even of its surroundings, to any large extent. However the $3\rightarrow1$ and $3\rightarrow-1$ transitions are broad because vibrations are excited. It follows that the redistribution of charge which accompanies a $2\rightarrow1$ transition also ought to excite vibrations. Therefore the absorption peaks corresponding to transitions to the $^3\Gamma_3$, $^3\Gamma_3'$, $^3\Phi_2$, $^3\Delta_1$, $^3\Pi_0'$, and $^3\Pi_0$ states of the plutonyl ion should all be broad. By analogy with the neptunyl ion the widths at half maximum should be about 1000 cm^{-1} [18].

The first prominent feature of the absorption spectrum above 14,000 cm^{-1} is the sharp peak at 16,075 cm^{-1}. Because of its sharpness this peak cannot be associated with any of the states listed in the previous paragraph. It is a moot question, but one which is crucial for our analysis, whether or not the 16,075 cm^{-1} peak rests on a broad base. If so, the strength of the underlying peak may be as large as 5. It would then be reasonable to associate this broad peak with transitions to $^3\Gamma_3$ and $^3\Gamma_3'$.

A serious difficulty then arises: It becomes necessary to associate the strong, broad peaks at 19,100 and 21,200 cm^{-1} with transitions to $^3\Phi_2$ and $^3\Delta_1$, respectively. The observed separation of the peaks is 2100 cm^{-1} but the calculated separation is about 4000 cm^{-1} and cannot be significantly reduced by any reasonable adjustment of the parameters.

Because of this difficulty [19] we consider it more likely that the nearly degenerate $^3\Gamma_3$ and $^3\Gamma_3'$ states should be identified with the broad peak at 19,000 cm^{-1}. The principal difficulty now is that there are only three calculated levels in the region between 14,000 and 19,000 cm^{-1} but the absorption curve indicates the presence of transitions to at least four states.

TABLE 2. *Observed and calculated absorption spectrum of the* $(PuO_2)^{++}$ *ion*

Level	Purity[a]	Position in cm⁻¹		$\epsilon_{max.}$	Width at half max. in cm⁻¹	Strength[b]	Composition of wave function by $|m_l|$ value				Calculated strength[c]
		Calc.	Exptl.				3	2	1	0	
³H₄	0.9249	0	0				0.9526	1.0180	0.0295	0.0000	
Σ₀	.7331	2445									
Π₁	.5929	4258									
³H₅	.9825	7133									
³Π₀′ (3, −2)	.9580	10157	10185	10.2	150	~5.7	.9617	0.9993	.0385	.0005	0.8860 (2→−2)+0.0350 (3→−1)
Σ₁	.5966	10489	10500	22.2	195	16.	.6953	1.2645	.0395	.0008	.4091 (3→−2)+.1499 (2→−3)+.0216 (2→−1)
³Π₀ (3, −2)	.6281	10640	10700	~4.4	~160	~2.5	.6518	1.3295	.0143	.0043	.5916 (2→−2)
³Π₂ (3, −2)	.9204	11892	12037	300.	34	31.	.9579	0.9623	.0788	.0009	.8517 (3→−3)
³H₆	.9278	12862	12660	2.7	400	3.	1.0680	.9318	.0000	.0000	< 0.01
³H₆′	.9580	12866					1.0686	.9312	.0002	.0000	< 0.01
¹Γ₄ (2, 2)	.8068	15469	15420	0.6	~200?	~0.3?	0.1130	1.7539	.1330	.0000	.0931 (gnd)
Σ₀	.9720	15980	16075	~5.	~135	~1.6	1.1555	0.7877	.0564	.0004	.0229 (3→−1)
Σ₁′	.6328	17877	17800	2.7	~600	~3.	1.2731	.6989	.0267	.0012	.1540 (3→−2)+.4301 (2→−3)
³Γ₃	.8828	19080	19100	11.	~1100	~24.	0.8978	.1022	.9840	.0159	.8170 (2→1)
³Γ₃′	.8838	19086					.8981	.1018	.9842	.0157	.8179 (2→1)
Σ₀	.8102	19780	19810	~7.	~80	~1.	.8681	1.0141	.1136	.0042	.0901 (3→−1)+.0999 (2→−2)
³Φ₂ (2, 1)	.8584	21253	21200	14.	~1200	~30.	.0959	0.8874	.9957	.0209	.7938 (3→1)
¹H₅	.8935	21885	21840	~7. ?	~300	~4.	1.0028	.8986	.0985	.0000	.0120 (1→2)+.0407 (2→3)
Π₁	.6660	23063					1.1679	.7183	.1125	.0011	.0227 (3→−2)+.2926 (2→−3)
Δ₂	.7349	23153					0.7780	.2504	.9580	.0136	.1037 (3→1)+.0380 (3→−3)
³Γ₄	.8381	24527					.8745	.1750	.9453	.0052	.0229 (gnd)
¹I₆	.9301	24780					1.9294	.0704	.0001	.0000	.0125 (1→3)
¹I₆′	.9310	24781					1.9310	.0689	.0000	.0000	.0125 (→3)
³Δ₁ (3, −1)	.8506	24917					0.9302	.1416	.9233	.0048	.7870 (2→−1)

[a] By "purity" we mean the extent to which the level can be characterized by the designation in column 1.
[b] The formula used in computing the strength is given in footnote 12.
[c] See the appendix.

When the $^3\Gamma_3$ states are placed at 19,000 cm⁻¹ the broad peak at 21,200 cm⁻¹ can readily be identified with transitions to the $^3\Phi_2|2-, 1->$ state.

With the dominant peaks in the spectrum at least tentatively identified we can refine out estimates of the various parameters, repeat the calculations, and then try to identify the remaining absorption peaks.

It appears that the narrow peaks at 16,075 and 19,810 cm⁻¹ should be associated with transitions to states that are predominantly Σ_0. This assignment is reasonable in view of the positions, widths and strengths of the two peaks.

We associate the peaks at 15,420, 17,800, and 21,840 cm⁻¹ with transitions to $^1\Gamma_4$, Π_1, and $^1H_5$ states, respectively. These assignments are all dubious and are made only because there are no alternatives. $^1\Gamma_4$ is in the right position but it appears fairly broad in figure 1 whereas the calculations indicate it should be narrow. Also its calculated strength would be negligible were it not for the fact that its wave function contains some of the same zero-order states as the ground state wave function.

The Σ_1 state whose calculated position is 17,877 cm⁻¹ should be narrow and perhaps half as strong as Σ_1 at 10,500 cm⁻¹. It is possible that the Π_1 state is an unresolved part of the large absorption peak at 19,100 cm⁻¹.

The difficulty with the $^1H_5$ assignment is that the calculated strength seems to be too small.

We have now discussed all calculated levels from 10,000 to 23,000 cm⁻¹. There is however one more observed peak at 16,950 cm⁻¹. We are not entirely convinced that this peak exists since it seems to be located by a single point on the most detailed figure in the paper of Connick et al. [20], and disappears when the HCl concentration is increased.

It is possible that both the 16,950 (if real) and the 17,800 cm⁻¹ peaks are associated with the major peak at 19,100 cm⁻¹ in the same way as the ripples on the low energy side of the neptunyl absorption peaks are associated with the strong 19,100 and 21,100 cm⁻¹ peaks.

The observations and the calculations on the plutonyl ion are summarized in table 2. See the appendix for an explanation of the right hand side of the table.

4. The $(NpO_2)^+$ Spectrum

The $(NpO_2)^+$ ion, like the $(NpO_2)^{++}$ ion, is believed to be linear. The optical absorption spectrum of the $(NpO_2)^+$ ion in aqueous solution has striking similarities to that of the $(PuO_2)^{++}$ ion so we shall assume that $(NpO_2)^+$ is an ion of the uranyl type and attempt to interpret its properties on this basis. It has already been mentioned that the asymmetric stretching frequency for the $(NpO_2)^+$ ion is lower than for the neptunyl or plutonyl ions. Also, the $(NpO_2)^+$ spectrum, as compared with the plutonyl spectrum, is shifted toward the red. We attribute these shifts to a weakening of the molecular field, to a lower value of the spin-orbit coupling constant, and to lower values of the Coulomb integrals for the $(NpO_2)^+$ ion.

The solution absorption spectrum of the $(NpO_2)^+$ ion is shown in figure 2. We regard the identification of the following absorption peaks as nearly certain:

8953 cm⁻¹	$^3\Pi_0'$
9146	Σ_1
9780	$^3\Pi_0$
10208	$^3\Pi_2$

TABLE 3. *Observed and calculated absorption spectrum of the* $(NpO_2)^+$ *ion*

Level	Purity[a]	Position in cm⁻¹ Calc.	Position in cm⁻¹ Exptl.	$\epsilon_{max.}$	Width at half max. in cm⁻¹	Strength[b]	Composition of wave function by $|m_l|$ value 3	2	1	0	Calculated strength[c]
³H₄	0.9216	0	0				.9626	.9991	.0382	0.0000	
Σ₀	.6920	2475									
Π₁	.6181	3893									
³H₅	.9115	6148	6173	3.5	47	1.2	.9692	1.0093	.0215	.0000	0 .0333 (3→−2) + 0.0186 (1→2) + 0.8400 (+→−)
³Π′₀ (3,−2)	.8380	8725	8953	5.8	55	1.3	.9483	.9943	.0570	.0003	.7723 (2→−2) + .0523 (3→−1)
³Σ₁	.6492	9450	9146	22.4	137	13.	.8301	1.1163	.0530	.0006	.3704 (3→−2) + .2332 (2→−3) + .0350 (2→−1)
³Π₀ (3,−2)	.4804	9862	9780	7.7	83	2.5	.7417	1.2427	.0129	.0027	.4486 (2→−2)
³Π₂ (3,−2)	.8503	10294	10208	> 82	< 139	45?	.9250	.9311	.1427	.0011	.7851 (3→−3)
vib			10970	2.1	93	0.7					
³H′₆	.8225	11171	11160	0.5	~ 150	~ 0.3	1.0627	.9274	.0098	.0000	.0876 (2→−2)
³H₆	.7076	11199					1.0213	.9753	.0028	.0006	.1352 (2→−2)
³Γ′₃	.9122	12949					.9301	.0700	.9901	.0099	.8410 (2→1)
³Γ₃	.9162	12969	13020	2.1	~ 900	~ 9.	.9315	.0685	.9908	.0091	.8447 (2→1)
Σ₀	.9006	13894	13824	< 0.5	~ 200	< 0.3	1.1547	.6680	.1754	.0020	.0739 (3→−1) + .0103 (1→−3)
¹Γ₄ (2, 2)	.6550	14345	14577	2.4	80	0.5	.1897	1.5267	.2835	.0001	.0814 (gnd)
³Σ₁	.5931	15911	16220	~ 9	160	> 5.5	1.0743	.8651	.0592	.0014	.2132 (3→−2) + .3155 (2→−3)
³Φ₂ (2, 1)	.6598	16045	16100	< 7.6	~ 700	~ 11.	.2906	.7095	.9838	.0159	.6081 (3→1) + .0232 (3→−3)
Δ₂ (3,−1)	.4482	16907	16906	~ 1.6	~ 150	~ 0.5	.6535	.4065	.9355	.0047	.2733 (3→1) + .0451 (3→−3)
Σ₀	.7912	17169					.7888	1.0511	.1570	.0030	.1288 (3→−1) + .0524 (2→−2)
³Δ₁	.5633	18085	18116	2.3	~ 1000	~ 5.	.9953	.2706	.7339	.0003	.0318 (2→−3) + .5202 (2→−1)
³Γ₄	.6659	18149					.8568	.2518	.8866	.0047	.0229 (gnd) + .0125 (3→−3) + .0135 (3→1)
¹H₅	.3654	18589					.9410	.5942	.4620	.0029	.0585 (2→−3) + .2540 (2→−1) + .0128 (2→3)
Π₁	.5895	19452	19360?	≳ 0.3	~ 500	~ 0.3	.7486	.7760	.4707	.0047	.0902 (2→−3) + .0271 (2→−1)
³Φ₃ (2, 1)	.8810	20337					.0993	.9008	.9937	.0064	.0394 (2→1) + .0182 (3→2)
³Φ′₃ (2, 1)	.9240	20425					.0554	.9446	.9961	.0039	.0509 (2→1) + .0191 (3→2)
¹Γ′₆	.9216	20532					1.9205	.0785	.0012	.0000	.0140 (1→3)
¹Γ₆	.8782	20578					1.8369	.1580	.0049	.0003	.0133 (1→3)
Π₁	.7665	21359	21008	6.4	320	3.7	.5242	.8574	.6020	.0164	.1465 (2→−3) + .0498 (3→−2)
³Δ′₃ (2, 1)	.9811	21841					.9976	.0024	.9907	.0093	< .01
³Δ₃ (2, 1)	.9289	21912	21700?	3.5?	~ 800	~ 5.	.9525	.0475	.9925	.0075	.0155 (2→1)
³Π′₀ (2,−1)	.9220	22380	22600	5.6	~ 700	~ 7.	.0664	.9872	.9342	.0122	.8497 (3→−1) + .0595 (2→−2)
³Π₀ (2,−1)	.6347	23397	23400	8.7	~ 800	~ 11.	.2989	.9586	.7327	.0098	.5858 (3→−1) + .0582 (2→−2)
³Γ₅	.7056	24292					.9954	.2835	.7212	.0000	.0102 (2→−1)
³Π₂ (2,−1)	.7623	24399					.2109	.7964	.9779	.0149	.0191 (3→−3)

[a] By "purity" we mean the extent to which the level can be characterized by the designation in column 1.
[b] The formula used in computing the strength is given in footnote 12.
[c] See the appendix.

The reasons for these assignments are the same as those for the corresponding assignments for the plutonyl ion. There are two small difficulties here which keep us from being completely certain about the assignments. (1) The peak at 9146 cm⁻¹ has a curious top [2] which makes it look as though it might be two unresolved peaks. (2) The ³Π₀ peak is stronger than the ³Π′₀ peak. Since ³Π′₀ is more nearly a pure state the reverse should be true, as is the case for the plutonyl ion. However, it is difficult (impossible ?) to find an interpretation of the peak which is alternative to the one given above.

The peak at 6173 cm⁻¹ is due primarily to the magnetic dipole transition from ³H₄ to ³H₅. The strength of this peak, calculated according to the formula given in III is 1.2; for a pure magnetic dipole transition the strength should be 1.0. It is rather unusual to find a line in a solution absorption spectrum that can be identified as due to a magnetic dipole transition. The calculated position of the ³H₅ peak is very near the observed position so we regard the identification of this peak as certain.

There are two small peaks at 10,970 and 11,160 cm⁻¹ in the (NpO₂)⁺ spectrum. If one of them is assigned to the ³H₆ states and the other to excitation of a vibrational mode the energy associated with the vibration would have to be 760 or 950 cm⁻¹. We do not have any direct information on the symmetric stretching frequency for the (NpO₂)⁺ ion in aqueous solution. However we note that according to the data of Jones [16], and of Jones and Penneman [3], the ratio of the asymmetrical stretching frequencies for (NpO₂)⁺ and (NpO₂)⁺⁺ in solution is 824/969 while the ratio of the asymmetrical stretching frequencies in solution and in a crystalline solid is 969/934. Therefore we estimate that the energy of the stretching vibration should be (824/969) × (969/934) × (energy of symmetric stretching vibration in a crystalline solid). The latter number [16] is 844 cm⁻¹ so our estimate for the energy of the symmetric stretching vibration of the (NpO₂)⁺ ion in aqueous solution is 745 cm⁻¹. We therefore associate the peak at 10,970 cm⁻¹ with a combined electronic and vibrational transition and the peak at 11,160 cm⁻¹ with the transitions to the ³H₆ and ³H′₆ states.

As in the case of the plutonyl ion we do not regard our identification of any of the remaining peaks in the (NpO₂)⁺ spectrum as certain. Generally speaking, our procedure in this case was the same as before: we interpreted the relatively strong, broad peaks as due to the "allowed" transitions to the ³Γ₃, ³Φ₂, ³Δ₁, and ³Π₀ (2,−1) states. We found that parameters could be chosen so that the calculated positions of these states agreed with the observed positions of strong, broad peaks insofar as they could be determined.

We believe one of these peaks definitely exists and is centered at 13,020 cm⁻¹. We ascribe it to transitions to the ³Γ₃ and ³Γ′₃ states. We place the next broad peak somewhat arbitrarily at 16,100 cm⁻¹. It

lies under the fairly sharp, strong peak at 16, 220 cm^{-1}. We associate the broad peak with the $^3\Phi_2$ state. The plots we have made with expanded abscissa reveal the structure much more clearly than figure 2 does.

The third broad peak is at about 18, 120 cm^{-1}. We identify it as being due to transitions to the $^3\Delta_1$ state.

The peak at 21,010 cm^{-1} is too narrow to be associated with a major redistribution of charge. It appears to rest on the low energy side of a broad peak centered at about 21, 700 cm^{-1}. There are two more broad peaks at about 22, 600 and 23, 400 cm^{-1}. We identify two of these three peaks with transitions to the $^3\Pi_0'$ (2, −1) and $^3\Pi_0$ (2, −1) states. The most plausible identification of the remaining peak is achieved if the $^3\Pi_0'$ and $^3\Pi_0$ states correspond to the peaks at 22, 600 and 23, 400 cm^{-1}, respectively. The remaining peak at 21, 700 cm^{-1} must then be ascribed to transitions to $^3\Delta_3$ and $^3\Delta_3'$ states. The principal objection to these assignments is that the experimental strength of the 21, 700 cm^{-1} peak is greater than the calculated strength for transitions to $^3\Delta_3$ states.

Another possibility is that some of the structure observed above 20, 000 cm^{-1} is due to excitation of the vibrational modes of the (NpO$_2$)$^+$ ion.

With all the broad peaks now identified plausibly but not certainly we consider the remaining features of the (NpO$_2$)$^+$ absorption spectrum. We ascribe the moderately strong 16, 220 cm^{-1} peak to transitions to a Σ_1 state and the 21, 010 cm^{-1} peak to transitions to a Π_1 state. These assignments are reasonable in terms of calculated position, strength and charge distribution, and in relation to the width and strength of the $^3\Sigma_1$ peak at 9146 cm^{-1}.

We identify the peak at 14,577 cm^{-1} with the $^1\Gamma_4$ (2, 2) state. The corresponding transition has a calculated strength different from zero only because the $^1\Gamma_4$ state contains the same zero order wave functions as the ground state. The 14,577 cm^{-1} peak is narrower than we expect for $^1\Gamma_4$ on the basis of the calculated charge distribution. The identification is therefore, rather unsatisfactory. However, the only other state in the vicinity is a Σ_0. It is difficult to adjust the parameters so that Σ_0 lies in the correct position.

We ascribe the two small peaks at 13,824 and 16,906 cm^{-1} to transitions to Σ_0 and Δ_2 states, respectively. Again, the assignments are reasonable in terms of calculated position, strength and charge distribution.

The very small peak at 19,360 cm^{-1} may be due to transitions to the $^1H_5$ state or a Π_1 state.

5. Values of the Parameters

The values of the parameters used in the final calculations on (NpO$_2$)$^+$ and (PuO$_2$)$^{++}$ are given in table 4. It is gratifying that X, Y, Z, and V$_6$ have values that are consistent with expectations based on our analysis of the (NpO$_2$)$^{++}$ spectrum in III. Also, the Coulomb integrals are larger for the (PuO$_2$)$^{++}$ than for the (NpO$_2$)$^+$ ion. This behavior is what one would expect since the higher nuclear charge for (PuO$_2$)$^{++}$ pulls the electrons in toward the center more and therefore increases their Coulomb repulsion.

The parameters ζ and L are probably determined to within 5 percent. The levels below 13,000 cm^{-1} that we regard as almost certainly identified depend principally on ζ and L and enable us to fix their values fairly closely. A is probably determined to within 10 percent by minimizing the mean square deviation for as many levels as we can reasonably identify.

TABLE 4. *Values of the Parameters*

	(NpO$_2$)$^+$	(PuO$_2$)$^{++}$
	cm^{-1}	cm^{-1}
X	253	− 1183
Y	12034	16793
Z	48555	49650
V_6	807	168
ζ	2090	2467
L	919	934
A	4322	5926
B	184	36
F_2	219. 5	254. 2
F_4	41. 21	41. 05
F_6	4. 677	6. 413

The value of B is determined largely by the position of the $^1\Gamma_4$ (2,2) level. As indicated above we are not at all sure we have located this level. We therefore estimate that B is known only within a factor of 2.

We started the calculations with $V_6 \sim 1000$ cm^{-1}. For both (NpO$_2$)$^+$ and (PuO$_2$)$^{++}$ we were forced to reduce this value substantially in order to minimize the rms deviations. It is difficult to estimate the accuracy of the determination of V_6 because the assumption of sixfold symmetry about the axis may be a drastic simplification.

Similarly we started the calculation with $Z \sim 35,000$ cm^{-1} and were forced to raise it to mimimize the rms deviations. Of all the levels below 25, 000 cm^{-1} $^3\Phi_2$ (2,1) depends most sensitively on Z. However ΔE ($^3\Phi_2$) ~ 0.03 ΔZ so one sees that Z is probably not very closely determined by the positions of these low levels.

The values given for X and Y depend on whether we have correctly located and identified the broad, strong peaks in the absorption spectra. If we assume that both the locations and the identifications are correct then the accuracy of determination of X and Y is probably ± 300 cm^{-1}.

For the (PuO$_2$)$^{++}$ ion the rms deviation between the calculated and the observed positions of 12 peaks is 150 cm^{-1}. The deviation was calculated from the formula:

$$\Delta^2 = \sum_i (\Delta E_i)^2/(n-8)$$

n is the number of observed levels and 8 is the number of parameters. Actually this formula may exaggerate the deviation because physical requirements limit one's freedom in adjusting the parameters. Also,

a more refined variational calculation than we used would undoubtedly enable one to choose parameters that would decrease the rms deviation somewhat. The 150 cm^{-1} deviation is comparable with the deviation of 125 cm^{-1} that Sugar [22] gives for the levels of the free Pr^{3+} ion.

For the (NpO$_2$)$^+$ ion the rms deviation between the calculated and the observed positions of the 14 peaks used to fix the parameters is 272 cm^{-1}. If we include also the $^3\Delta_3$, $^3\Pi_0'$ (2, -1) and $^3\Pi_0$ (2, -1) peaks the rms deviation is 241 cm^{-1}.

6. Conclusion

We have shown how the solution absorption spectra of the (NpO$_2$)$^+$ and (PuO$_2$)$^{++}$ ions can be interpreted on the basis of exact calculations and plausible arguments concerning the strength and width of the absorption peaks. To confirm the interpretation it would be of some value to locate experimentally the two peaks for (NpO$_2$)$^+$ that lie below 6,000 cm^{-1} and the three peaks for (PuO$_2$)$^{++}$ that lie below 9,000 cm^{-1}. Further to check the theory developed here it is highly desirable to obtain the low temperature absorption spectra of a crystalline plutonyl compound and of a Np (V) compound. A study of the Zeeman effect would be helpful.

We think the parameters and their variations among the ions (NpO$_2$)$^{++}$, (NpO$_2$)$^+$ and (PuO$_2$)$^{++}$ are now sufficiently well known so that a theoretical investigation of the absorption spectrum of the (AmO$_2$)$^{++}$ ion could be undertaken. Also, by combining the information gained from studying NpF$_6$ and the (PuO$_2$)$^{++}$ ion, it should be possible to interpret the spectrum of PuF$_6$.

7. Appendix

In analyzing the spectra it is useful to have some quantitative ideas, however crude they may be, concerning the relative breadths and strengths of the absorption peaks that correspond to the various calculated energy levels. One then has some basis for judging whether or not it is reasonable to associate a calculated level with an observed absorption peak. We have developed a method which gives us some insight into this problem.

In the ground state the electrons are predominantly in states with $m_l = \pm 3$ and ± 2. If in the excited state the electrons are still predominantly in the ± 3 and ± 2 states we assume that the absorption peak will be narrow. On the other hand, if in the excited state there is an appreciable probability that the $m_l = \pm 1$, 0 orbitals are occupied, then we assume the absorption peak will be broad. We can calculate from the eigenvectors the distribution of charge over the various orbital states. These calculations have been made and the results are given in table 2 for the (PuO$_2$)$^{++}$ ion and in table 3 for the (NpO$_2$)$^+$ ion.

Now suppose we have two states Ψ and Φ between which a transition can take place. Due to the various interactions each one of these states will be a complicated mixture of the zero order states. Let us therefore write

$$\Psi = a\psi_a + b\psi_b + c\psi_c + \ldots$$

$$\Phi = \alpha\psi_\alpha + \beta\psi_\beta + \gamma\psi_\gamma + \ldots$$

Here the $\psi_a, \ldots, \psi_\alpha, \ldots$ denote the zero order states and $a, \ldots, \alpha, \ldots$ are appropriate numerical coefficients. Suppose the transition from ψ_a to ψ_α is "allowed"; that is, suppose ψ_a and ψ_α differ in, at most, the value of m_l for one electron. For example, ψ_a might be $^3H_4|3-, 2->$ and ψ_α might be $^3\Pi_2|-3, 2->$. Similarly, suppose the transition from ψ_b to ψ_β is "allowed," etc. We then take as a quantitative estimate of the strength of the peak corresponding to the Ψ to Φ transition

$$a^2\alpha^2 (\psi_a \rightarrow \psi_\alpha) + b^2\beta^2 (\psi_b \rightarrow \psi_\beta) + \ldots$$

The bracketed quantities denote the probabilities for the indicated transitions.

This device is useful in estimating the relative strengths of transitions that would be forbidden if the states were pure, but which are somewhat "allowed" because of the complicated mixing of the states which actually occurs. The numbers $a^2\alpha^2$, $b^2\beta^2$, etc., have been calculated and are given in tables 2 and 3 when they exceed 0.01.

The estimates of relative strengths obtained in this way can conceivably be improved by using empirical information which may be available. For example, the strengths of the observed neptunyl lines at 6752 and 8168 cm^{-1}, calculated according to the formula in the appendix to III, are about 7.7 and 39, respectively. The former corresponds principally to a $3 \rightarrow -2$ transition: the latter to a $3 \rightarrow -3$ transition. The ratios of the strengths of these two transitions should therefore be about 1:5. We would expect the relative strengths of the $3 \rightarrow -2$ and $3 \rightarrow -3$ transitions for the (NpO$_2$)$^+$ and (PuO$_2$)$^{++}$ ions also to be in the approximate ratio 1:5. The ratio seems to be closer to 1:3 but the difference is perhaps not surprising in view of the crudeness of the assumptions made. Also there may be real differences between the one- and the two-electron cases.

8. References and Notes

[1] J. C. Eisenstein and M. H. L. Pryce, Proc. Roy. Soc. A229, 20 (1955). This paper (to be referred to here as II) contains a brief reference to the (NpO$_2$)$^+$ ion which, like (PuO$_2$)$^{++}$, is believed to be of the uranyl type.

[2] J. C. Eisenstein and M. H. L. Pryce, J. Res. NBS 69A (Phys. and Chem.) No. 3, 217 (1965). This paper will be referred to as III.

[3] L. H. Jones and R. A. Penneman, J. Chem. Phys. **21**, 542 (1953).

[4] See J. C. Eisenstein, J. Chem. Phys. **39**, 2128 (1963), table IV. It must be conceded that there are peculiar variations from ion to ion but they may be due to differences in the approximations made in the calculations.

[5] K. A. Kraus, F. Nelson, and G. J. Johnson, J. Am. Chem. Soc. **71**, 2510 (1951).

[6] E. U. Condon and G. H. Shortley, Theory of Atomic Spectra, Cambridge University Press (1935).

[7] E. C. Ridley, Proc. Roy. Soc. **A243**, 422 (1958).

[8] Here, and in what follows, we shall designate the states by their principal components. We use the normal spectroscopic notation for linear molecules in Russell-Saunders coupling in so far as possible. Since there is no Greek letter corresponding to H we denote states with $\Lambda = 5$ by the Roman letter H. These states should not be confused with the H-states of atomic spectroscopy. The zero-order states are sometimes so extensively mixed that no spin assignment can be made.

[9] Actually the $|3-, 2->$ and the $|-2+, -3+>$ states are degenerate. All states for which $\Sigma m_j = 1$ or 2 (mod 6) have a twofold degeneracy. We shall not make any further explicit reference to this degeneracy.

[10] B. Bleaney, P. M. Llewellyn, M. H. L. Pryce and G. R. Hall, Phil. Mag. **45**, 991 (1954).

[11] C. A. Hutchison and W. B. Lewis, Phys. Rev. **95**, 1096 (1954).

[12] The method of calculating strengths is described in the appendix of III. We assume that the formula

$$\text{strength} = 37.9 \ \epsilon_{max} \Delta\nu / \nu_0$$

which is appropriate to peaks with a Gaussian shape can be used.

[13] The same is true for the pairs of $^3\Pi_0$ states:

$$|2-, -1->, \ |1+, -2+> \text{ and } |1-, 0->, \ |0+, -1+>.$$

[14] This shoulder is barely discernible in figure 1. However it shows up clearly when the data are plotted on a scale with expanded abscissa.

[15] The mixing of the zero-order states for the neptunyl ion by the spin orbit interaction and the part of the ligand field with sixfold symmetry makes it impossible to determine the relative probabilities for the $3 \rightarrow -3$ and the $3 \rightarrow -2$ transitions. The $(NpO_2)^{++}$ absorption peak at 6752 cm^{-1} which is due mostly to the $3 \rightarrow -2$ transition has strength 7.7. The absorption peak at 8168 cm^{-1} which is due mostly to the $3 \rightarrow -3$ transition has strength 39.

[16] L. H. Jones, J. Chem. Phys. **23**, 2105 (1955).

[17] The apparent degeneracy of the states $^3\Gamma_3|3-, \ 1->$ and $^3\Gamma_{-3}|-1+, \ -3+>$ is removed by the component of the ligand field which has sixfold symmetry. Contrary to the situation for $^3\Pi_0$ and $^3\Pi_0'$ no significant distinction can be made between $^3\Gamma_3$ and $^3\Gamma_3'$.

[18] We say 1000 rather than 1600 cm^{-1} because the $3 \rightarrow -3$ and $3 \rightarrow -2$ transitions are narrower for the plutonyl than for the neptunyl ion.

[19] Difficulties in identifying the less prominent peaks also arise if we place $^3\Gamma_3$ at 16,000 cm^{-1}.

[20] R. E. Connick, M. Kasha, W. H. McVey, and G. E. Sheline, The Transuranium Elements, National Nuclear Energy Series, IV, 14b, paper 4.20 (McGraw-Hill Book Co., New York, 1949).

[21] We have located this peak at 9146 cm^{-1}. Actually the extinction coefficient has its maximum value at 9124 cm^{-1}. The structure at the top of this peak is hardly noticeable in figure 1 but becomes apparent when the scale for the abscissa is expanded.

[22] J. Sugar, Phys. Rev. Letters **14**, 731 (1965).

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