

Article

Vibrational Spectra and Normal Framework Coordinate Analysis of Uranyl Bis(2-Hydroxy-1-Naphthaldehyde)

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Os espectros infravermelho e Raman com transformada de Fourier do composto sólido urânio bis(2-hidroxi-1-naftaldeído), têm sido medidos na região entre 4000-70 cm⁻¹. Usando a correlação D_{2h} → C_{2v}, os modos vibracionais fundamentais dos ligantes foram atribuídos aproximadamente. Para atribuir o espectro do esqueleto do complexo em estudo, foi possível fazer a mesma correlação entre outros complexos do íon urânio com o urânio bis(2-hidroxi-1-naftaldeído). Calculamos as constantes de força para o esqueleto deste composto.

The Fourier transform infrared and Raman spectra of solid uranyl bis(2-hydroxy-1-naphthaldehyde) are measured in the 4000-70 cm⁻¹ region. Using the correlation D_{2h} → C_{2v}, the fundamental ligand vibrational modes were tentatively assigned. The same correlation could be made among other another uranyl complexes with the uranyl bis(2-hydroxy-1-naphthaldehyde) to assign the framework spectra. Force constants for the framework of this compound are calculated.

Keywords: uranyl bis(2-hydroxy-1-naphthaldehyde), vibrational spectra, force constants

Introduction

Recently we published the IR and Raman spectra of solid uranyl 2,4-pentanedionate, UO₂(acac)₂¹, uranyl bis(1,3-diphenyl-1,3-propanedionate), UO₂(HBDM)₂, and uranyl bis(1,1,1-trifluoro-2,4-pentanedionate), UO₂(HBTF)₂². We also reported two alternative sets of symmetry coordinates for UO₂(acac)₂³. Normal vibrational calculations were also made for the infrared and Raman active vibrational modes of the framework of UO₂(acac)₂, UO₂(HBDM)₂ and UO₂(HBTF)₂². Raman, resonance Raman, and infrared spectra of potassium uranyl croconate were also studied by Gonçalves, Oliveira and Santos⁴, who concluded that in terms of vibrational frequency shifts, the UO₂⁺² moiety behaves as an isolated oscillator. In order to study the influence of a higher resonant ligand on the UO₂⁺² ion, the present work is devoted to a thorough interpretation of the infrared (IR) and Raman vibrations of uranyl bis(2-hydroxy-1-naphthaldehyde), hereafter abbreviated as UO₂(2H1N)₂, for which no pre-

vious IR or Raman spectra nor vibrational analysis have been reported. In our study we carried out a normal coordinate analysis for the skeletal fundamentals assuming a local C_{2v} symmetry, on the assumption of a modified valence force field.

Experimental

UO₂(2H1N)₂ was prepared according to the synthesis proposed by Gómez Lara⁵. For the preparation of UO₂(2H1N)₂, we mixed in stoichiometric quantities of an alcoholic solution of 2-hydroxy-1-naphthaldehyde with an aqueous solution of uranyl acetate. The product contained 38.89% uranium, which corresponds to 38.90% for the theoretical composition of uranium in the compound of formula C₂₂H₁₄O₆U. The IR spectra of polycrystalline UO₂(2H1N)₂ between 4000 and 310 cm⁻¹ with a resolution of 2 cm⁻¹, were measured on a NICOLET 55X from Nujol mulls placed between KBr plates, and those between 700 and 70 cm⁻¹ were measured on a NICOLET 740 FT-IR spectrometer with a resolution of 0.3 cm⁻¹, using a deuter-

ated tryglycine sulfate (DTGS) detector with polyethylene windows, and an Ever - Glo™ Mid-Far IR (9600 - 50 cm⁻¹) source. In this case the sample was mixed with polyethylene powder and pressed to form a pellet. The IR spectra between 210-70 cm⁻¹ show a non-definable shape, probably due to the source used in the measurements. Therefore, only the coincident bands with the Raman spectra were tentatively assigned. Raman spectra of the solid samples were run on a NICOLET FT-Raman 910 spectrometer, using 1064.0 nm radiation from a Nd-YAG laser. The resolution for the Raman spectra was 2.0 cm⁻¹. The spectrometer had a germanium detector. In our compound, the crystals did not exhibit the appropriate size and crystallinity to perform polarization measurements in the solid state. Some difficulties were found in recording the Raman spectrum in saturated CHCl₃ solution.

Results and Discussion

Vibrational irreducible representations

Assuming a C_{2v} symmetry for the UO₂(2H1N)₂ complex, the 3n-6 = 123 vibrational modes can be classified among the symmetry species:

$$\Gamma_{\text{vib}} = 42a_1 (\text{IR,R}) + 20a_2 (\text{R}) + 21b_1 (\text{IR,R}) + 40b_2 (\text{IR,R})$$

Band assignments

Infrared and Raman ν(C-H) stretching modes. The IR and Raman vibrational representation for the ν(C-H) stretching modes can be classified in the symmetry species $\Gamma_{\nu(\text{CH})} = 6a_1 + 6b_2$. In the region of 3200-3000 cm⁻¹ in the IR spectra we observed bands with very weak intensities. None of these bands could be assigned. In the Raman spectra we observed weak Raman shifts which can be assigned as 3086 cm⁻¹ (b₂), 3067 cm⁻¹ (a₁), and 3046 cm⁻¹ (a₁). Three shoulders of very weak intensities appear at 3014, 2999 and 2989 cm⁻¹, which were assigned as 1615 cm⁻¹ (R)(b₂) + 1417 cm⁻¹ (R)(b₂) = 3032 cm⁻¹ (a₁), 2 x 1508 cm⁻¹ = 3016 cm⁻¹ (a₁), and 1586 cm⁻¹ (IR,R)(a₁) + 1417 cm⁻¹ (R)(b₂) = 3003 cm⁻¹ (a₁). The ν_s(CH) and ν_{as}(CH) out of the naphthalene rings were tentatively assigned in the Raman spectrum at 2923 cm⁻¹ (a₁) and 2986 cm⁻¹ (b₂).

The IR and Raman ν(C=C) stretching, β(CCH) and γ(CCC) bendings of the naphthalene rings. These vibrational modes can be classified according the representations: $\Gamma_{\nu(\text{C=C})} = 11a_1 + 11b_2$, $\Gamma_{\beta(\text{CCH})} = 6a_1 + 6b_2$ and $\Gamma_{\gamma(\text{CCC})} = 6a_1 + 6b_2$, respectively.

These vibrational modes appear as the coupling vibrations of the ΔQ(C=C), Δβ(CCH), and Δγ(CCC) internal coordinates. Only a complete normal coordinate analysis could give information about the percentage of the contribution of each internal coordinate to the normal mode. Our

approximate assignments were based on the following criteria⁶: 1) In the region of 1650-1400 cm⁻¹, the ΔQ(C=C) internal coordinates make a higher contribution to the normal mode; 2) Bendings β(CCH) in aromatic rings appear in a wide region as coupling modes (see, for example, the spectra of benzene^{7,8}, toluene^{9,10,11}, p-xylene^{12,13}, and naphthalene⁶). From this comparative analysis we can conclude that for the UO₂(2H1N)₂ complex, in the region of 1628 to 1000 cm⁻¹, we could find coupled normal modes ν(C=C) + β(CCH) + γ(CCC), in which from 1628 to 1417 cm⁻¹ the fundamental bands have a higher contribution from the Q(C=C) internal coordinates. From 1145 cm⁻¹ to 750 cm⁻¹, the higher contribution must be from the bendings Δβ(CCH) + Δγ(CCC) internal coordinates. The correlation D_{2h} → C_{2v} between naphthalene and UO₂(2H1N)₂, to assign a particular symmetry type in the normal mode, could be made only for the a_{1g} → a₁ and b_{2u} → b₂. Our tentative assignments are given in Table 1.

Out of plane vibrational modes ρ(CH) and χ(CCCC) of the naphthalene rings. These vibrational modes can be worked out according to the following symmetries: $\Gamma_{\rho(\text{CH})} = 6a_2 + 6b_1$ and $\Gamma_{\chi(\text{CCCC})} = 6a_2 + 6b_1$. Sverdlov *et al.*⁶ summarize the assignment of the IR and Raman out-of-plane vibrational modes for naphthalene. In comparison, for the UO₂(2N1H)₂ complex we have assigned the following frequencies (in cm⁻¹) to the ρ(CH) and χ(CCCC) modes: 976 (R), 972 (IR)(b₁) ρ(CH); 947 (R), 949 (IR)(b₁) ρ(CH); 898 (R)(a₂) χ(CCCC); 863 (R), 866 (IR)(b₁) ρ(CH); 825 (R), 822 (IR)(b₁) ρ(CH); 737 (R), 739 (IR)(b₁) ρ(CH); 594 (R)(a₂) χ(CCCC); 575 (R)(a₂) χ(CCCC); 491 (R), 490 (IR)(b₁) χ(CCCC); 457 (R), 454 (IR)(b₁) χ(CCCC); 419 (R)(a₂) χ(CCCC); 388 (R)(a₂) χ(CCCC); 373 (IR,R)(b₁) χ(CCCC); 369 (R)(a₂) χ(CCCC); 359 (R), 360 (IR)(b₁) χ(CCCC) and 341 (R), 340 (IR)(b₁) χ(CCCC) or 2 x 174 = 348 (a₁).

Coupling vibrational modes between the ligands and the UO₂⁺⁺ ion. These vibrational modes can be classified according to the irreducible representations: $\Gamma_{\nu(\text{C=O})} = 2a_1 + 2b_2$, $\Gamma_{\nu(\text{C=C})} = a_1 + b_2$, $\Gamma_{\nu(\text{C-H})} = a_1 + b_2$, $\Gamma_{\beta(\text{CCH})} = a_1 + b_2$, $\Gamma_{\delta(\text{CCO})} = a_1 + b_2$, $\Gamma_{\delta(\text{CCO})} = a_1 + b_2$ and $\Gamma_{\chi} = 5a_2 + 5b_1$. The assignments, discussed later and summarized in Table 1, have been proposed on the basis of the analogy of some Raman shifts and IR frequencies of UO₂(acac)₂ with the UO₂(2H1N)₂ complex. The correlation D_{2h} → C_{2v} between these uranyl complexes was also made to assign the symmetry of a particular mode. Thornton assignments¹⁴ for the ν(C=O) modes of β-ketoenol complexes of Ni(II), Cu(II), and Zn(II) were found at 1605, 1577, and 1598 cm⁻¹, respectively, and the vibrational frequencies found at 1260, 1272, and 1258 cm⁻¹, were assigned predominantly to the ν(C=C) stretching modes of the Ni(II), Cu(II) and Zn(II)

Table 1. Frequencies (cm^{-1}) and experimental assignments for the infrared and Raman spectra of the $\text{UO}_2(2\text{H1N})_2$ complex.

Raman	Infrared	Approximate Description	Raman	Infrared	Approximate Description
3086		$\nu(\text{CH})(b_2)$		774 (sh)	$538 + 243 = 781$
3067		$\nu(\text{CH})(a_1)$	769		$454 + 320 = 774$
3046		$\nu(\text{CH})(a_1)$	752	755	$\gamma(\text{CCH})$
3014		$1615 + 1417 = 3032$	737	739	$\rho(\text{CH})(b_1)$
3000		$2 \times 1508 = 3016$		734 (sh)	$373 + 369 = 742$
2982		$1586 + 1417 = 3003$		700	$360 + 340 = 700$
2923		$\nu(\text{CH})(a_1)$	690	690	$\delta(\text{COU})(b_2)$
2896		$\nu(\text{CH})(b_2)$	654	654	$\delta(\text{COU})(a_1)$
1627		$\nu(\text{C}=\text{C})(a_1)$	594		$\chi(\text{CCCC})(a_2)$ $\chi(\text{CCCO})(b_1)$
	1615	$\nu(\text{C}=\text{C})(b_2)$		585	
1606	1604	$\nu(\text{C}=\text{C})(b_2)$	575		$\chi(\text{CCCC})(a_2)$ $\chi(\text{CCCO})(b_1)$
1586	1585	$\nu(\text{C}=\text{O})(a_1)$		560	
1538	1535	$\nu(\text{C}=\text{C})(b_2)$		550	$\nu_{\text{as}}(\text{UO})_{\text{eq.}}(b_2)$
1507	1508	$\nu(\text{C}=\text{O})(b_2)$	537	538	$\nu_{\text{s}}(\text{UO})_{\text{eq.}}(b_2)$
1451		$\nu(\text{C}=\text{C})(a_1)$	491	490	$\chi(\text{CCCC})$
1432		$\nu(\text{C}=\text{C})$	457	454	$\chi(\text{CCCC})$
	1417	$\chi(\text{C}=\text{C})$	434	435	$\nu_{\text{s}}(\text{UO})_{\text{eq.}}(a_1)$
1379		$\chi(\text{C}=\text{O})(b_2)$	419 (sh)		$\chi(\text{CCCC})$
1363	1364	$\chi(\text{C}=\text{C})$	406	409	$\nu_{\text{s}}(\text{UO})_{\text{eq.}}(a_1)$
1338	1338	$\chi(\text{C}=\text{C})$		394	$261 + 140 = 401$
1303	1302	$\chi(\text{C}=\text{C})$	388		$\chi(\text{CCCC})(a_2)$
1273	1273	$\nu(\text{C}=\text{C})(a_1)$		382	$216 + 172 = 388$
1251	1251	$\beta(\text{CCH})$	373	373	$\chi(\text{CCCC})(b_1)$
1215	1214	$\beta(\text{CCH})$	369		$\chi(\text{CCCC})(a_2)$
1184	1184	(CCH)	359	360	$\chi(\text{CCCC})(b_1)$
1161	1159	$\beta(\text{CCH})$	341	340	$2 \times 174 = 348$ or $\chi(\text{CCCC})(b_1)$
1143	1145	(CCH)	330	331	$174 + 161 = 335$
1098		$2 \times 550 = 1100$	319	320	$\chi(\text{CCCC})(b_1)$
1086	1087	$\beta(\text{CCH})$	296	296	$159 + 140 = 299$
	1073	$538 + 550 = 1088$	285	285	$\chi(\text{CCCO})(b_1)$
1039	1040	$\beta(\text{CCH})$	273		$\lambda(\text{OUO})(a_2)$
999	1001	$\beta(\text{CCH})$	260	261	$\lambda(\text{OUO})(a_1)$
976	972	$\rho(\text{CH})(b_1)$	251	251	$\alpha(\text{OUO})(a_1)$
947	949	$\rho(\text{CH})(b_1)$	246		$\lambda(\text{OUO})(a_2)$
920	924	$\nu_{\text{as}}(\text{UO})_{\text{axial}}(b_1)$		243	$\lambda(\text{OUO})(b_2)$
898		$\chi(\text{CCCC})(a_2)$	216	216	$\lambda(\text{OUO})(b_1)$
863	866	$\rho(\text{CH})(b_1)$	198	196	$\omega(\text{OUO})(a_1)$
837	841	$\nu_{\text{i}}(\text{UO})_{\text{axial}}(a_1)$	182		$\chi(\text{CCCO})(a_2)$
825	822	$\rho(\text{CH})(b_1)$	174	172	$\chi(\text{CCCO})(b_1)$
	800	$\rho(\text{CH})(b_1)$	169		$\chi(\text{CCCO})(a_2)$
784	785	$\rho(\text{CH})(a_1)$	161	159	$\chi(\text{CCCO})(b_1)$
				140	$\lambda(\text{OUO})(b_1)$

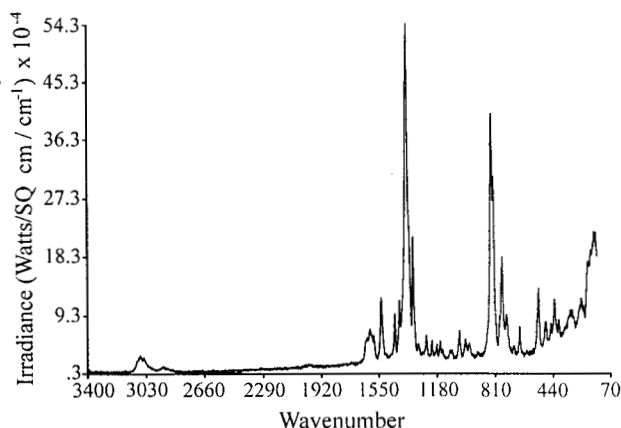


Figure 1. Raman spectrum of $\text{UO}_2(2\text{H1N})_2$.

acetylacetonate complexes. These findings together with Junge and Musso's¹⁵ assignments for the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ stretchings for $\text{Pd}(\text{II})$ -acetylacetonate and $\text{Cu}(\text{II})$ -acetylacetonate, and with our assignments for $\text{UO}_2(\text{acac})_2$ ¹, can be summarized as (frequencies in cm^{-1}):

	$\nu_{\text{as}}(\text{C}=\text{O})$	$\nu_{\text{s}}(\text{C}=\text{O})$	$\nu_{\text{as}}(\text{C}=\text{C})$	$\nu_{\text{s}}(\text{C}=\text{C})$
Ni(II)- β -ketoenol		1605		1260
Cu(II)- β -ketoenol		1577		1272
Zn(II)- β -ketoeno		1598		1258
Pd(II)-acetylacetonate	1378	1555	1520	1276
Cu(II)-acetylacetonate	1397	1578	1527	1275
$\text{UO}_2(\text{acac})_2$	1385	1576	1520	1271

In our work, the Raman and IR active frequencies found at 1586 cm^{-1} in $\text{UO}_2(2\text{H1N})_2$ were assigned to the stretching $\nu(\text{C}=\text{O})(a_1)$. This frequency correlates with the 1576 cm^{-1} b_{1u} frequency found in the uranyl acetylacetonate complex. The frequencies at 1538 cm^{-1} (R) and 1535 cm^{-1} (IR) were assigned to the $\nu(\text{C}=\text{C})$ (b_2) in $\text{UO}_2(2\text{H1N})_2$, which correlates with the 1520 cm^{-1} (IR) (b_{2u}) frequency of $\text{UO}_2(\text{acac})_2$. The other correlations that we could make between the Raman and IR fundamental frequencies of these uranyl complexes were 1381 cm^{-1} (b_{3g}) and 1385 cm^{-1} (b_{2u}) with the 1379 cm^{-1} (IR) assigned as $\nu(\text{C}=\text{O})$ (b_2) stretching mode; 1270 (b_{3g}) and 1271 (b_{1u}) with 1273 cm^{-1} (IR,R) assigned as $\nu(\text{C}=\text{C})$ (a_1); 797 cm^{-1} (b_{3u}) with 800 cm^{-1} assigned as the $\rho(\text{CH})$ (b_1) out-of-plane; 658 cm^{-1} (b_{3g} , b_{1u}) with 690 cm^{-1} (IR,R) assigned as the angular (b_2) deformation of the internal ring $\delta(\text{CCO})$; 651 cm^{-1} (b_{1u}) with 654 cm^{-1} (IR, Raman) assigned to the $\delta(\text{CCO})$ (a_1); 570 cm^{-1} (b_{3u}) with 585 cm^{-1} assigned as the torsion mode $\chi(\text{CCCO})$ (b_1); 559 cm^{-1} (b_{1g} or b_{2g}) with 560 cm^{-1} (IR) assigned to the $\chi(\text{CCCO})$ (b_1) torsion. The frequency 180 cm^{-1} (b_{3u}) correlated with 182 cm^{-1} (R, sh) and was assigned as another torsion mode of (a_2) symmetry.

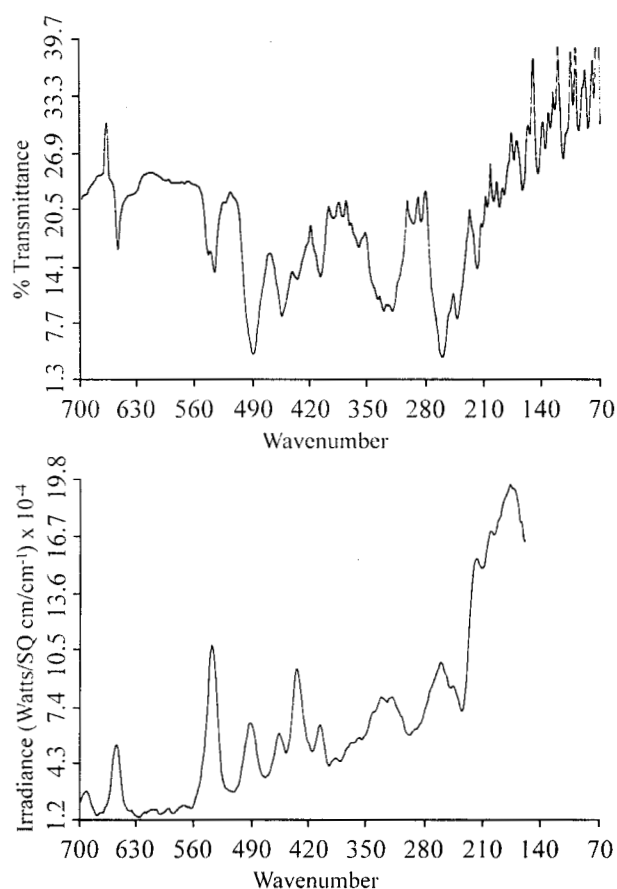


Figure 2. Low region IR and Raman spectra ($700\text{--}70 \text{ cm}^{-1}$) of $\text{UO}_2(2\text{H1N})_2$.

The Raman shift found at 156 cm^{-1} (b_{1g} or b_{2g}) correlated with 161 cm^{-1} (R) and 159 cm^{-1} (IR) and was assigned as the $\chi(\text{CCCO})$ (b_1) torsion. The other attributions were 285 cm^{-1} (IR,R)(b_1) $\chi(\text{CCCO})$, 174 (R), 172 cm^{-1} (IR)(b_1) $\chi(\text{CCCO})$, and 169 cm^{-1} (R)(a_2) $\chi(\text{CCCO})$.

Normal framework modes. The normal modes for the $[\text{UO}_2\text{O}_4]$ skeletons of $\text{UO}_2(2\text{H1N})_2$ can be distributed among the following symmetry species:

$$\Gamma_{\text{vib}} = 6a_1(\text{IR,R}) + 2a_2(\text{R}) + 3b_1(\text{IR,R}) + 4b_2(\text{IR,R})$$

The framework band assignment of the crystalline compound was made for comparison with uranyl complexes of D_{2h} symmetry [1, 2]: $\text{UO}_2(\text{acac})_2$, $\text{UO}_2(\text{HDBM})_2$ and $\text{UO}_2(\text{HBTF})_2$. The correlation $D_{2h} \rightarrow C_{2v}$ was used to assign particular symmetries to the normal modes. Table 1 presents the experimental assignment for the whole complex.

ν (U-O) stretching modes. The vibrational representation for the different (U-O) stretching modes can be classified as $\Gamma_{\text{U=O}} = a_1 + b_1$ and $\Gamma_{\text{U-O}} = 2a_1 + 2b_2$. Axial $\nu_{\text{as}}(\text{U=O})(b_{3u})$ frequencies for $\text{UO}_2(\text{acac})_2$, $\text{UO}_2(\text{HDBM})_2$,

and $\text{UO}_2(\text{HBTF})_2$ were found at 921, 908, and 926 cm^{-1} , respectively. For $\text{UO}_2(2\text{H1N})_2$, the IR and Raman bands found at 920 cm^{-1} and 924 cm^{-1} were attributed to $\nu_{\text{as}}(\text{U}=\text{O})(b_1)$. The $\nu_{\text{s}}(\text{U}=\text{O})(a_1)$ found at 841 cm^{-1} (IR), coincident with 837 cm^{-1} (R), correlated with 836 cm^{-1} (a_g), 830 cm^{-1} (a_g), and 836 cm^{-1} (a_g) of $\text{UO}_2(\text{acac})_2$, $\text{UO}_2(\text{HDBM})_2$ and $\text{UO}_2(\text{HBTF})_2$, respectively. The following assignments were given for the equatorial $\nu(\text{U}-\text{O})$ stretching of $\text{UO}_2(2\text{H1N})_2$: 435 cm^{-1} (IR) and 434 cm^{-1} (R) to the $\nu_{\text{s}}(\text{U}-\text{O})(a_1)$; 409 cm^{-1} (IR) and 406 cm^{-1} (R) to the $\nu_{\text{s}}(\text{U}-\text{O})(a_1)$. The $\nu_{\text{as}}(\text{U}-\text{O})$ were found at 550 cm^{-1} (IR) (b_2) and at 537 cm^{-1} (R), 538 cm^{-1} (IR) (b_2). These frequencies correlated with the $\nu_{\text{as}}(\text{U}-\text{O})$ of the other uranyl complexes which were used as a reference to assign the frequencies.

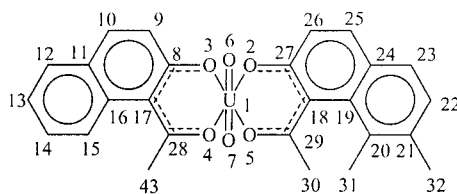
Axial $\lambda(\text{OUO})$ and equatorial $\omega(\text{OUO})$ and $\alpha(\text{OUO})$ bending vibrations. These normal modes can be worked out according to the following symmetries: $\Gamma_{\text{bend}} = 3a_1(\text{IR,R}) + 2a_2(\text{R}) + 2b_1(\text{IR,R}) + 2b_2(\text{IR,R})$, which can be subdivided as: $\Gamma_{\lambda} = a_1 + 2a_2 + 2b_1 + b_2$, $\Gamma_{\alpha} = a_1$, and $\Gamma_{\omega} = a_1 + b_2$. Our assignments correlate to the IR and Raman frequencies attributed to $\text{UO}_2(\text{acac})_2$, $\text{UO}_2(\text{HDBM})_2$, and $\text{UO}_2(\text{HBTF})_2$.²

The observed frequencies and the approximate assignments are listed in Table 1.

Normal coordinate analysis

A normal coordinate analysis for the framework structure of uranyl bis(2-hydroxy-1-naphthaldehyde) was car-

ried out to aid the assignment of the observed frequencies. The molecular structure and the internal coordinates for $\text{UO}_2(2\text{H1N})_2$ are shown in Fig. 3. Geometrical parameters which describe the skeletal structure of $\text{UO}_2(2\text{H1N})_2$ were taken from Ref. 16 and the two pairs of planar angles OUO were chosen to be 87° and 93° . Symmetry coordinates which describe the framework vibrations were constructed³ for the $[\text{UO}_2\text{O}_4]$ framework of D_{2h} symmetry. To use this set of symmetry coordinates for a $[\text{UO}_2\text{O}_4]$ framework of C_{2v} symmetry, we have applied a correlation $D_{2h} \rightarrow C_{2v}$ to them. A modified general valence force field (MGVFF) potential function was used and the initial set of diagonal force constant values in each symmetry type was transferred from the force field of $\text{UO}_2(\text{acac})_2$.³ Force constants were adjusted to give the best frequency fit by a least squares method developed by Miyazawa¹⁷ and Shimanochi¹⁸, using computer programs which have been previously reported¹⁹. The final valence force constant values are $f(\text{UO})_{\text{axial}} = 6.87 \pm 0.16 \text{ m dyn } \text{\AA}^{-1}$ and $f(\text{UO})_{\text{eq.}} = 2.36 \pm 0.13 \text{ m dyn } \text{\AA}^{-1}$ for the U-O axial and equatorial bonds. Our result of 6.87 $\text{m dyn } \text{\AA}^{-1}$ as in the cases of $\text{UO}_2(\text{acac})_2$, $\text{UO}_2(\text{HDBM})_2$ and $\text{UO}_2(\text{HBTF})_2$,² reflects a lowering of the axial electron density through the effect of coordination with the 2-hydroxy-1-naphthaldehyde ligands. The value of $f(\text{UO})_{\text{eq.}} = 2.36 \text{ m dyn } \text{\AA}^{-1}$ in $\text{UO}_2(2\text{H1N})_2$, compared to the mean value of 1.79 $\text{m dyn } \text{\AA}^{-1}$ obtained for $\text{UO}_2(\text{acac})_2$, $\text{UO}_2(\text{HDBM})_2$, and $\text{UO}_2(\text{HBTF})_2$, reflects the resonance effect in the equatorial U-O bonds. Also, assuming a single



Normal mode	Internal coordinate	Atoms				Normal mode	Internal coordinate	Atoms			
		i	j	k	l			i	j	k	l
$\nu(\text{CH})$	$\Delta r_i (i = 1 - 12)$	20	31			$\gamma(\text{CCC})$	$\Delta \gamma_i (i = 1 - 24)$	11	12	13	
$\nu(\text{CH})$	$\Delta r_i (i = 1, 2)$	29	30			$\delta(\text{CCO})$	$\Delta \delta_i (i = 1, 2)$	17	8	3	
$\nu(\text{C}=\text{C})$	$\Delta Q_i (i = 1 - 22)$	11	12			$\delta(\text{CCO})$	$\Delta \delta_i (i = 1, 2)$	17	28	4	
$\nu(\text{C}=\text{O})$	$\Delta q_i (i = 1, 2)$	8	3			$\lambda(\text{OUO})$	$\Delta \lambda_i (i = 1 - 6)$	2	1	6	
$\nu(\text{C}=\text{O})$	$\Delta p_i (i = 1, 2)$	28	4			$\omega(\text{OUO})$	$\Delta \omega_i (i = 1, 2)$	3	1	4	
$\nu(\text{C}=\text{C})$	$\Delta t_i (i = 1, 2)$	17	28			$\alpha(\text{OUO})$	$\Delta \alpha_i (i = 1, 2)$	2	1	3	
$\nu(\text{U}=\text{O})$	$\Delta u_i (i = 1, 2)$	1	6			$\rho(\text{CH})$	$\Delta \rho_i (i = 1, 12)$	19	20	21	31
$\nu(\text{U}-\text{O})$	$\Delta u_i (i = 1 - 4)$	1	2			$\rho(\text{CH})$	$\Delta \rho_i (i = 1, 2)$	17	28	4	43
$\beta(\text{CCH})$	$\Delta \beta_i (i = 1 - 24)$	21	20	31		$\chi(\text{CCCC})$	$\Delta \chi_i (i = 1 - 22)$	13	12	11	16
$\beta(\text{CCH})$	$\Delta \beta_i (i = 1 - 4)$	17	28	43		$\chi(\text{CCCU})$	$\Delta \chi_i (i = 1 - 4)$	17	8	3	1

Figure 3. Molecular structure and internal coordinates for $\text{UO}_2(2\text{H1N})_2$. As an example, only one internal coordinate of each type is described.

oscillator for the U-O equatorial bond, the uranium-oxygen bond order can be calculated by Gordy's equation²⁰:

$$f = 1.67N_{\text{UO}}(\chi_{\text{U}}\chi_{\text{O}}/d^2)^{3/4} + 0.30$$

where **f** is the U-O force constant, **N** is the bond order, **d** is the U-O bond length, and χ_{U} and χ_{O} are the U and O atom electronegativities. Using the Allred and Rochow²¹ elec-

Table 2. Symmetry and valence force constants for the [UO₂O₄] skeleton of UO₂(2H1N)₂.

Symmetry Force Constants	Analytical Expression	Value
a ₁	$F_{11} = f_{\text{u}} + f_{\text{uu}}$	6.65 ± 0.20
	$F_{22} = f_{\text{u}'} + 2f_{\text{u}'\text{u}'} + f_{\text{u}'\text{u}'^*}$	1.53 ± 0.04
	$F_{33} = f_{\text{u}} - f_{\text{u}'\text{u}'^*}$	1.62 ± 0.10
	$F_{44} = f_{\lambda} + f_{\lambda\lambda\text{op}}$	0.66 ± 0.16
	$F_{55} = f_{\alpha}$	1.26 ± 0.06
	$F_{66} = f_{\omega} + f_{\omega\omega}$	1.16 ± 0.06
a ₂	$F_{77} = f_{\lambda} - 2f_{\lambda\lambda} + f_{\lambda\lambda\text{op}}$	0.54 ± 0.00
	$F_{88} = f_{\lambda} - 2f_{\lambda\lambda\text{a}} + 2f_{\lambda\lambda\text{aop}} - f_{\lambda\lambda\text{op}}$	1.01 ± 0.01
b ₁	$F_{99} = f_{\text{a}} - f_{\text{aa}}$	7.09 ± 0.11
	$F_{1010} = f_{\lambda} + 2f_{\lambda\lambda\text{a}} - f_{\lambda\lambda\text{aop}} - f_{\lambda\lambda\text{op}}$	0.26 ± 0.03
b ₂	$F_{11}F_{11} = f_{\lambda} - 2f_{\lambda\lambda} + f_{\lambda\lambda\text{op}}$	0.36 ± 0.02
	$F_{12}F_{12} = f_{\text{u}} - f_{\text{uu}}$	2.57 ± 0.01
	$F_{13}F_{13} = f_{\text{u}} - 2f_{\text{uu}} + f_{\text{uu}^*}$	2.72 ± 0.07
	$F_{14}F_{14} = f_{\lambda} - f_{\lambda\lambda\text{op}}$	0.58 ± 0.02
	$F_{15}F_{15} = f_{\omega} - f_{\omega\omega}$	0.84 ± 0.01
	Valence force constants	
$f_{\text{u}} = f_{(\text{U}=\text{O})}$		6.87 ± 0.16
$f_{\text{u}'} = f_{(\text{U}-\text{O})\text{equatorial}}$		2.36 ± 0.06
$f = f_{(\text{OUO})\text{axial}}$		0.42 ± 0.04
$f_{\alpha} = f_{(\text{OUO})\text{equatorial}}$		1.26 ± 0.06
$f_{\omega} = f_{(\text{OUO})\text{equatorial}}$		1.00 ± 0.04
$f_{\text{uu}} = f_{(\text{UO}/\text{UO})\text{axial}}$		-0.22 ± 0.16
$f_{\text{u}'\text{u}'} = f_{(\text{UO}/\text{UO})\text{equatorial}}$		0.30 ± 0.06
$f_{\text{u}'\text{u}'^*} = f_{(\text{UO}/\text{UO})\text{equatorial}^*}$		-0.24 ± 0.04
$f_{\omega\omega} = f_{(\text{OUO}/\text{OUO})\text{equatorial}}$		-0.16 ± 0.04
$f_{\lambda\lambda} = f_{(\text{OUO}/\text{OUO})\text{axial}}$		-0.11 ± 0.04
$f_{\lambda\lambda\text{a}} = f_{(\text{OUO}/\text{OUO})\text{axial}}$		-0.11 ± 0.04
$f_{\lambda\lambda\text{op}} = f_{(\text{OUO}/\text{OUO})\text{axial}}$		-0.20 ± 0.04
$f_{\lambda\lambda\text{aop}} = f_{(\text{OUO}/\text{OUO})\text{axial}}$		0.06 ± 0.04

Stretching force and valence force constants are in mdyN Å⁻¹, and the bending force constants are in mdyN Å (for a definition of the internal coordinates, see Fig. 3. In the valence force constants, op = opposite; a = adjacent; aop = adjacent and opposite).

tronegativities and Mulliken's method²², we obtained the following values for the bond order of the U-O bonds in the UO₂(2H1N)₂, UO₂(acac)₂, UO₂(HDBM)₂, and UO₂(HBTF)₂ complexes:

	N _{UO} (Allred-Rochow)	N _{UO} (Mulliken)
UO ₂ (2H1N) ₂	1.07	1.05
UO ₂ (acac) ₂ , UO ₂ (HBTF) ₂ and UO ₂ (HDBM) ₂	0.77	0.76

These values also reflect the strong influence of the 2-hydroxy-1-naphthaldehyde ligand on the equatorial coordination with the oxygen atoms of the UO₂⁺² ion.

The potential energy distribution revealed that the $\nu_{\text{as}}(\text{U}=\text{O})$ and $\nu_{\text{s}}(\text{U}=\text{O})$ are pure vibrational modes. The skeletal equatorial bendings $\alpha(\text{OUO})$ and $\omega(\text{OUO})$ are strongly coupled in the vibrational modes belonging to the a₁ symmetry. The agreement between observed and calculated frequencies is within 0.1 %. The final sets of symmetry and valence force constants for the [UO₂O₄] framework are presented in Table 2.

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