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Calculation of harmonic and anharmonic vibrational wavenumbers for triatomic uranium compounds XUY

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Abstract

The performance of nine different variants of density functional theory (DFT) for the calculation of the vibrational frequencies of the triatomic compounds UO_2^{2+} , NUN, NUO^+ and CUO is investigated and compared with the predictions obtained with the CASPT2 method [Chem. Phys. Lett. 331 (2000) 229]. Vibrational anharmonicity is calculated for UO_2^{2+} and for CUO and is shown to be small for these systems. A detailed comparison of experimental data obtained in rare-gas matrices with the DFT predictions shows that while the performance of hybrid DFT is uneven, the more “elementary” GGA versions such as PW91 perform extremely well, as the estimated unsigned (signed) average errors are only 11 (–2) cm^{-1} for the five observed IR bands. Overall, the DFT/GGA results for the closed-shell compounds considered here are at least as good as those yielded by the CASPT2 method, which is computationally much more demanding. Calculated IR intensities are in at least semi-quantitative agreement with experiment. We suggest that the vibrational data becoming available for actinide compounds could and should be used to obtain more reliable parameters in hybrid versions of DFT. The calculated harmonic stretching force constants are shown to depend critically on the U–X bond length, but they are almost insensitive to the method used for their calculation, at a given distance. Observed vibrational spectra can therefore be used to infer reliable bond lengths.

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Keywords: Density functional theory; Vibrational spectra; Vibrational anharmonicity; Actinide chemistry; Spin–orbit coupling

1. Introduction

There is intense current interest in the application of computational methods to the study of actinide compounds. The coordination chemistry of the actinides is important for both fundamental and practical reasons; it is fascinatingly different from that displayed by elements located in other parts of the periodic table, and a better understanding of the factors that control this behaviour will help work directed towards the treatment

of radioactive nuclear wastes. If quantum chemical methods are to be applied with confidence, it is clearly essential to be able to anticipate the reliability that can reasonably be expected. This reliability will have to be demonstrated by comparison with secure experimental data [1]. For this reason, the series of closed-shell triatomic XUY molecules recently characterized by Andrews and co-workers (NUN, NUO^+ and CUO) [2,3] plays a pivotal role; iso-electronic with the uranyl dication, UO_2^{2+} , which dominates the high-oxidation-state chemistry of uranium but for which no experimental data are yet available for the isolated ion, they provide a data set that can be used to calibrate the performance of different theoretical methods. Since vibrational frequencies are delicate probes of bonding and are highly sensitive to geometry, it is clear that any method that

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cannot yield satisfactory frequencies for the entire set does not have general applicability.

We have previously shown that density functional methods (DFT), combined with quasi-relativistic pseudopotentials (RECP), yield structural and vibrational parameters for the uranyl ion that are in good agreement with those obtained from highly correlated (CCSD(T)) four-component (fully relativistic) methods [4], but at a small fraction of the computational expense. In particular, the hybrid version of DFT known as B3LYP was judged to be the most reliable, though differences between B3LYP [5] and B3PW91 [6] are relatively slight. A clear account of the different variants of DFT (local-density approximation or LDA), those that adopt the gradient-corrected approximation or GGA (“second generation”) and the hybrid versions that contain some Hartree–Fock exchange (“third generation”), together with summaries of their performance for molecules containing light atoms, may be found in [7]. We have also shown that B3LYP predictions for the vibrational wavenumbers of several open-shell oxide species derived from the uranyl di-cation, such as UO_2^+ , UO_2 and UO_2^- , are consistently close to the experimental data obtained from neon matrices [8]. However, we hesitate to include these open-shell systems in the present work, since standard DFT calculations take no account of spin–orbit coupling effects. Now spin–orbit coupling is primarily an atomic effect, so one might imagine that its effects on molecular properties other than the energy would be relatively small. We are aware of only two publications concerning actinide-containing polyatomic molecules in which these effects have been treated explicitly, and their conclusions differ markedly. In the case of UO_2 , Gagliardi and co-workers [9] have reported an appreciable influence on the $\text{U}=\text{O}$ bond length and a remarkably large change to the symmetric stretching vibrational frequency (an increase of 139 cm^{-1} , or 17%). But García-Hernández et al. [10] have found only marginal effects on both bond lengths and vibrational frequencies in their study of NpO_2^+ and NpF_6 . It is therefore not yet clear whether spin–orbit effects are likely in general to have a significant influence on vibrational frequencies.

In addition to our own earlier work [4], three other research groups have analyzed the performance of different computational methods for the vibrational frequencies of the uranyl ion [10–12]. Han and Hirao report that hybrid versions of DFT methods are more successful than either LDA or GGA, though the LDA is satisfactory for the stretching modes [12]. García-Hernández et al. [10] note that GGA versions underestimate stretching frequencies, but that B3LYP performs better. They consider that the LDA approach is satisfactory, when combined with all-electron methods that incorporate scalar relativistic effects. De Jong and co-workers assert that the hybrid B3LYP method is more successful than the LDA [11]. All three groups [10–12]

show that a pseudopotential approach is acceptable for uranium, providing that 32 electrons are treated explicitly (a “very small core”). Treatments that employ a “large core” of 78 electrons are less satisfactory. Even though these conclusions broadly agree with our own in [4], we are now inclined to question their usefulness, for two reasons. First, since experimental data for the isolated uranyl ion are not yet available, the conclusions are necessarily based on comparison with other calculations. Even though these were performed at a very high level of theory, it is clearly more satisfactory to be able to compare with secure experimental data. Second, they refer only to the uranyl ion, so it is not clear that the conclusions will be valid more generally.

Gagliardi and Roos [13] have advocated the use of the CASPT2 method for the calculation of vibrational frequencies. This method is more elaborate than DFT and it should provide a correct description of systems for which a single-reference treatment is inadequate. They were able to obtain satisfactory agreement with the observed matrix vibrational wavenumbers for both closed-shell (CUO, NUN and NUO⁺) and open-shell (NUO and UO_2^+) systems with the CASPT2 method, though the B3LYP version of DFT was shown to perform poorly for CUO, with errors as large as 101 cm^{-1} , or 9.6%. At the CASPT2 level, differences between calculated harmonic and observed matrix stretching wavenumbers with the “large” ANO basis on C, N or O range from -46 (NUN) to -14 (CUO) cm^{-1} , or always less than 4.3%; when two g-type functions are added to the U basis, the performance is improved, as the differences for NUN (one mode) and CUO (two modes) are reduced to only -5 , -9 and -3 cm^{-1} , respectively. While this agreement is impressive, we note that the CASPT2 method suffers from several weaknesses if its application to larger molecules is intended. We summarize these drawbacks here. Analytic gradients are not yet generally available, meaning that the calculation of vibrational frequencies is not normally practicable for any system containing more than a handful of atoms. Basis-set effects are *far* larger than for any version of DFT; this point is considered in detail in Section 4. And the scaling characteristics of CASPT2 calculations with the size of the active space are unfavourable: whether a moderately sized active space will be acceptable in a molecule containing more than a handful of atoms will obviously depend critically on the particular case.

Andrews and co-workers [3a] have published a DFT study of CUO that achieved astonishingly good agreement with experiment for the two vibrational stretching motions; differences between calculated harmonic and observed neon matrix values are only 2 cm^{-1} . The ADF computer code [14] used in that work differs from other programs in two important aspects; Slater-type functions are used rather than Gaussians, and the program explicitly treats all the electrons in the molecule rather than relying on pseudopotentials. The excellent agree-

ment with experiment that they achieved could be taken to imply that these differences are important, though one should note that different choices of the computational options available lead to differences in vibrational wavenumbers predicted for CUO of some 30 cm^{-1} , even though the same variety of DFT (PW91) was used [3b]. It may be significant that a GGA version of DFT was adopted by Andrews et al., whereas most workers prefer to use “hybrid” versions such as B3LYP (see [4,10–12]).

While these two recent papers [3a,13] lead to different conclusions as to the suitability of the “economical” DFT methods for actinide chemistry, it seemed to us that both are incomplete in some important respects. No information is available on several points that we feel must be considered, before an informed and balanced judgment can be given. Not necessarily in order of importance, the points include the following: the importance of any differences between matrix and gas-phase vibrational wavenumbers, the magnitude of vibrational anharmonicity, and the performance of a representative selection of the large variety of DFT versions now available, both GGA and hybrid, including the more recent functionals such as PBE, PBE0 [15] and B97 [16]. We note that PBE and PBE0 contain no empirical parameters, PBE0 being a hybrid version of PBE, but there are ten parameters in B97, compared to the three in B3LYP. While the superiority of “hybrid” DFT over GGA versions has been convincingly demonstrated for molecules containing relatively light atoms, for structural, vibrational and thermochemical properties [7,17], it is not clear that the same preference will also be found for systems where relativistic effects are crucial. We have therefore undertaken a systematic study of UO_2^{2+} , NUN, NUO^+ and CUO, using nine different versions of DFT, to obtain the equilibrium geometries and harmonic vibrational frequencies. We investigate the accuracy of the predicted IR intensities, where this is possible. We have also undertaken more refined calculations that go beyond the limitations of the harmonic approximation, for both UO_2^{2+} and CUO, to try to establish the extent of differences between observed and harmonic vibrational wavenumbers.

2. Computational methods

DFT calculations were undertaken with the Gaussian 98 [18] and NWChem [19] programs. We have used a variant of the local density approximation (LDA, known as SVWN5 in the Gaussian program), several functionals of the GGA type (BLYP, BPW91, PW91 and PBE) and several hybrid functionals (B97, B3LYP, B3PW91 and PBE0). As in our earlier work [4,8], pseudopotentials were adopted for all atoms, developed either in Stuttgart [20] (for uranium, 60 electrons in the core), or in Toulouse [21] (for C, N and O). Flexible

bases, approximately triple-zeta for U and double-zeta plus polarization plus diffuse for C, N and O, as described in detail elsewhere [4,8], were adopted for the “valence” electrons (32 for U, 4, 5 or 6 for C, N or O). “Ultra-fine” grids (99 radial shells and 590 angular points) were adopted with the Gaussian program, unless noted otherwise; we draw attention to the inadequacy of the default (“fine”) grids if reliable values are sought for calculated vibrational wavenumbers for these systems, as the differences between fine and ultrafine results are of the order of $5\text{--}10\text{ cm}^{-1}$ for the stretching modes (either increase or decrease), and as much as 25 cm^{-1} for the bending mode. A few tests with even finer grids (125 radial shells and 770 angular points) produced additional changes of only 1 cm^{-1} or less. Similar grids were used with the NWChem program (123 radial shells and 590 angular points).

In the quartic approximation the rotationless vibrational Hamiltonian can be written as:

$$H_v = \frac{1}{2} \sum_i \omega_i (p_i^2 + q_i^2) + \frac{1}{6} \sum_{ijk} \phi_{ijk} q_i q_j q_k + \frac{1}{24} \sum_{ijkl} \phi_{ijkl} q_i q_j q_k q_l + \sum_{\alpha} B_{\alpha} \left[\sum_{ij} \left(\frac{\omega_i}{\omega_j} \right)^{1/2} \xi_{ij}^{\alpha} q_i p_j \right]^2,$$

where q_i are dimensionless normal coordinates, p_i conjugated momenta and ω_i , ϕ_{ijk} , ϕ_{ijkl} , B_{α} and ξ_{ij}^{α} are the harmonic wavenumbers, cubic and quartic force constants, rotational constants and Coriolis constants, respectively.

In our case the last term, which is very small for these uranium compounds, is neglected. The potential energy function is transformed to reduced normal coordinates by performing a least-squares fit of $V(q_i q_j q_k q_l)$ to energies evaluated in curvilinear coordinates. In S_i space, the potential function is expressed in a Taylor series as:

$$V_{(s)} = \frac{1}{2} \sum_{ij} f_{ij} S_i S_j + \frac{1}{6} \sum_{ijk} f_{ijk} S_i S_j S_k + \frac{1}{24} \sum_{ijkl} f_{ijkl} S_i S_j S_k S_l + \dots$$

where f_{ij} , f_{ijk} and f_{ijkl} are, respectively, quadratic and quartic force constants and the kinetic part is determined by:

$$T = \frac{1}{2} \sum_{ij} g_{ij}(0) P_{S_i} P_{S_j} + \frac{1}{2} \sum_{ijk} g_{ijk} P_{S_i} S_k P_{S_j},$$

with $g_{ijk} = (\partial g_{ij} / \partial S_k)_0$ and where $g_{ij}(0)$ are the elements of the Wilson matrix for the equilibrium geometry [22]. Computations of the vibrational anharmonic contributions require up to the fourth derivative of the potential energy. In the case of UO_2^{2+} and CUO, the quartic force field was obtained from a least-squares fit performed to B3LYP energies on a grid of 81 points, corresponding to the distorted structures generated by bond and angular

displacements of 0.01 Å and 0.1 rad around the equilibrium structure. The values of the quadratic, cubic and quartic terms in curvilinear coordinates are obtained from a fourth-order polynomial fit. The rms errors and the maximum absolute error of the fit were 0.31 and 0.19 μE_H , and 2.10 and 2.31 μE_H , respectively, for UO_2^{2+} and CUO.

The method used to calculate the anharmonic wavenumbers of UO_2^{2+} and CUO in the medium IR region is based on a complete variational treatment presented elsewhere [23]. For all the anharmonic terms, the eigenvalues and eigenvectors of the corresponding vibrational levels are obtained by standard diagonalization of the Hamiltonian using the LAPACK package [24]. In our problem harmonic oscillator functions are used as expansion functions. About 1000 functions are needed to obtain the first 30 converged eigenvalues with an accuracy of 1 cm^{-1} .

3. Results

In Table 1, we present optimized bond lengths and harmonic vibrational frequencies for UO_2^{2+} , NUN, NUO^+ and CUO calculated with various functionals; linearity was imposed (but see below). The CASPT2 results of Gagliardi and Roos [13] are also presented for comparison. The calculated harmonic frequencies are compared with experimental results, both as observed in the rare-gas matrix and after “correction” according to

our estimates of matrix effects and vibrational anharmonicity (see the last column in Table 1); these estimations are described below. IR intensities were obtained within the double-harmonic approximation; these are briefly compared with the available experimental data in Section 4.

It is clearly important to consider the possible errors in our calculated vibrational frequencies due to basis-set incompleteness. We have previously reported [8] that extension of the U basis (addition of g- then h-type functions) produces only modest changes (a few cm^{-1}) in the vibrational wavenumbers for UO_2^{2+} using the B3LYP method. Comparable effects are found for CUO. If the pseudopotentials on C, N and O are replaced by all-electron bases of equivalent size, the changes in vibrational wavenumbers are again of the order of only 5 cm^{-1} . If the polarization bases on C, N or O are improved (single d to double d, then addition of f-type functions), the resulting changes in vibrational wavenumbers are again only about 5 cm^{-1} . As the different effects noted here are not systematically all of the same sign, either for a given molecule or for a given vibrational mode, we feel confident that our values reported in Table 1 are converged to about 10 cm^{-1} , for a given version of DFT. This level of precision is sufficient for our present purposes, in view of the uncertainties in the “corrections” due to matrix effects and to anharmonicity (see below).

While it is clearly not necessary to comment in detail on each entry in Table 1, a few general remarks are

Table 1

Harmonic vibrational frequencies in cm^{-1} and bond lengths in Å calculated with various functionals and compared with CASPT2 calculations [13], experimental data and corrected experimental data

		CASPT2	LDA	BLYP	BPW91	PW91	PBE	B97	B3LYP	B3PW91	PBE0	Exp	Corr Exp ^a
OUO^{2+}	$r(\text{UO})$	1.705 ^b	1.710	1.734	1.721	1.720	1.719	1.699	1.705	1.695	1.688		
	$\omega(\sigma_u)$	1066 ^b	1118	1060	1091	1093	1099	1155	1140	1162	1184		
	$\omega(\sigma_g)$	959 ^b	1015	956	987	989	996	1021	1041	1064	1088		
	$\omega(\pi_u)$		112	97	108	107	108	167	161	167	179		
NUN	$r(\text{UN})$	1.734 ^c	1.733	1.754	1.743	1.741	1.740	1.727	1.731	1.722	1.716		
	$\omega(\sigma_u)$	1072 ^c	1104	1053	1080	1083	1093	1130	1118	1136	1159	1077	1089
	$\omega(\sigma_g)$	1015 ^c	1050	997	1025	1029	1039	1083	1071	1090	1116		
	$\omega(\pi_u)$		34i	48i	37i	33i	70	110	102	106	119		
NUO^+	$r(\text{UO})$	1.746 ^b	1.749	1.775	1.761	1.760	1.759	1.742	1.749	1.740	1.732		
	$r(\text{UN})$	1.695 ^b	1.698	1.717	1.706	1.705	1.704	1.687	1.690	1.683	1.676		
	$\omega(\text{NU})$	1081 ^b	1155	1098	1129	1133	1140	1192	1183	1206	1228	1119	1134
	$\omega(\text{OU})$	942 ^b	987	934	962	965	970	1016	1000	1021	1042	970	979
	$\omega(\pi)$		52	32	49	46	93	133	124	130	141		
CUO	$r(\text{UO})$	1.790 ^c	1.793	1.824	1.810	1.809	1.808	1.796	1.802	1.792	1.785		
	$r(\text{UC})$	1.765 ^c	1.761	1.778	1.766	1.767	1.763	1.745	1.752	1.745	1.738		
	$\omega(\text{CU})$	1077 ^c	1105	1052	1086	1086	1102	1143	1132	1154	1182	1047	1062
	$\omega(\text{OU})$	870 ^c	895	844	866	868	870	901	889	905	922	872	881
	$\omega(\pi)$		25	32i	40i	32i	83	91	89	90	102		

^a See text for origin of corrections to experimental data.

^b CASPT2 results from [13], “large” ANO basis on C, N and O, no g-type function in U basis.

^c CASPT2 results from [13], “large” ANO basis on C, N and O, g-type functions included in U basis; results for NUN and CUO only.

Table 2

Comparison between computed harmonic vibrational frequencies and corrected experimental results for XUY linear systems: NUN; NUO⁺; CUO

Method	Err	Err	Max Err
B3LYP	35	35	70
B3PW91	55	55	92
B97	47	47	81
PBE0	77	77	120
BLYP	33	−33	−45
BPW91	14	−5	24
PW91	11	−2	24
PBE	14	6	40
LDA	20	20	43
CASPT2 (lg) ^a	14	−5	−17
CASPT2 (l) ^b	35	−33	−58

Error in cm^{−1} (theory–experiment).

^a CASPT2 results from [13], “large” ANO basis on C, N and O, g-type functions included in U basis; results for NUN and CUO only.

^b CASPT2 results from [13], “large” ANO basis on C, N and O, no g-type function in U basis.

appropriate. The addition of some HF exchange to a GGA-type version of DFT systematically increases *all* the vibrational frequencies. For the stretching modes, the increase is typically 60–90 cm^{−1}, though smaller increases are found for the lower-frequency mode in CUO. Comparing the different hybrid functionals, the vibra-

tional frequencies increase systematically in the order B3LYP < B3PW91 < PBE0; the same order is found for the corresponding GGA versions, BLYP < BPW91 < PBE. Results obtained with the hybrid B97 functional are usually close to the B3PW91 values. The choice of exchange functional appears to have little influence on the results, as the frequencies obtained by the BPW91 and PW91 versions differ by only a few cm^{−1}. The simplest form of DFT used here, the LD approximation, gives results intermediate between those characteristic of GGA and hybrid versions.

One particularly striking difference between GGA and hybrid results needs comment. If linearity is imposed, imaginary bending frequencies are found for NUN and CUO with all three GGA versions (see Table 1). The LD approach gives an imaginary frequency for NUN, but a real (though small) value for CUO. Hybrid functionals, however, give real bending frequencies for all the molecules in our sample, though these frequencies are always less than 180 cm^{−1}, and typically 80–120 cm^{−1} for NUN and CUO. If the linearity constraint is relaxed, the optimum bond angle for NUN is 171° (PW91), while the optimum angle for CUO lies between 166° and 172°, depending on the particular functional adopted. Use of an all-electron basis for N also gives a slight bending for NUN with GGA versions. The PW91

Table 3

Anharmonic wavenumbers calculated for the ground state of UO₂²⁺: dominant contributions for the lowest transitions

Name	Calculated wavenumbers (cm ^{−1})	Description	Name	Calculated wavenumbers (cm ^{−1})	Description
ν_1 (*)	1033.9	0.98(100)			
ν_2 (*)	1132.7	0.98(010)			
ν_3 (*)	169.5	1.00(001)			
$2\nu_3$	339.1	0.99(002)	$2\nu_1 + 4\nu_3$	2736.9	0.91(204) + 0.06(304)
$3\nu_3$	508.6	0.99(003)	$2\nu_2 + 3\nu_3$	2765.2	0.96(023)
$4\nu_3$	678.2	0.99(004)	$\nu_1 + \nu_2 + 4\nu_3$	2831.8	0.92(114) + 0.06(214)
$\nu_1 + \nu_3$	1202.6	0.97(101)	$2\nu_1 + 5\nu_3$	2904.7	0.90(205) + 0.06(305)
$\nu_2 + \nu_3$	1301.3	0.98(011)	$2\nu_2 + 4\nu_3$	2932.7	0.96(024)
$\nu_1 + 2\nu_3$	1371.3	0.97(102)	$\nu_1 + \nu_2 + 5\nu_3$	3025.7	0.92(115)
$\nu_2 + 2\nu_3$	1469.8	0.98(012)	$3\nu_1$	3094.9	0.86(300) + 0.09(400)
$\nu_1 + 3\nu_3$	1540.2	0.97(103)	$2\nu_2 + 5\nu_3$	3100.2	0.95(025)
$\nu_2 + 3\nu_3$	1638.4	0.98(013)	$2\nu_1 + \nu_2$	3187.3	0.85(210) + 0.09(310)
$\nu_1 + 4\nu_3$	1708.7	0.97(104)	$3\nu_1 + \nu_3$	3261.9	0.85(301) + 0.09(401)
$\nu_2 + 4\nu_3$	1806.8	0.98(014)	$\nu_1 + 2\nu_2$	3285.8	0.87(120) + 0.08(220)
$\nu_1 + 5\nu_3$	1877.3	0.96(105)	$2\nu_1 + \nu_2 + \nu_3$	3354.1	0.84(211) + 0.09(311)
$\nu_2 + 5\nu_3$	2017.7	0.97(015)	$3\nu_2$	3389.9	0.94(030)
$2\nu_1$	2065.5	0.93(200)	$3\nu_1 + 2\nu_3$	3428.9	0.84(302) + 0.09(402)
$\nu_1 + \nu_2$	2161.1	0.93(110)	$\nu_1 + 2\nu_2 + \nu_3$	3452.4	0.87(121) + 0.08(221)
$2\nu_1 + \nu_3$	2233.4	0.93(201)	$2\nu_1 + \nu_2 + 2\nu_3$	3521.0	0.84(212) + 0.10(312)
$2\nu_2$	2262.7	0.96(020)	$3\nu_2 + \nu_3$	3556.4	0.94(031) + 0.06(131)
$\nu_1 + \nu_2 + \nu_3$	2328.8	0.93(111)	$3\nu_1 + 3\nu_3$	3595.9	0.83(303) + 0.10(403)
$2\nu_1 + 2\nu_3$	2401.2	0.92(202)	$\nu_1 + 2\nu_2 + 2\nu_3$	3619.1	0.86(122) + 0.09(222)
$2\nu_2 + \nu_3$	2430.2	0.96(021)	$2\nu_1 + \nu_2 + 3\nu_3$	3687.8	0.83(213) + 0.10(313)
$\nu_1 + \nu_2 + 2\nu_3$	2496.5	0.93(112)	$3\nu_2 + 2\nu_3$	3722.9	0.93(032) + 0.06(132)
$2\nu_1 + 3\nu_3$	2569.1	0.92(203)	$3\nu_1 + 4\nu_3$	3762.9	0.82(304) + 0.1(404) + 0.06(204)
$2\nu_2 + 2\nu_3$	2597.7	0.96(022)	$\nu_1 + 2\nu_2 + 3\nu_3$	3785.8	0.85(123) + 0.09(223)
$\nu_1 + \nu_2 + 3\nu_3$	2664.1	0.92(113)			

Symmetry coordinates: $S_1 = 2^{-1/2}(R + R')$; $S_2 = 2^{-1/2}(R - R')$; $S_3 = \alpha$.

stretching frequencies calculated for NUN at its optimum C_{2v} geometry differ from the data in Table 1 by less than 1 cm^{-1} . Experimentally, only a single peak is seen in the IR spectrum of matrix-isolated NUN [2]. While the immediate conclusion is that NUN is linear, this deduction may be too hasty. The intensity calculated for the symmetric stretching mode at 171° (PW91) is only 0.4% of that for the antisymmetric mode. Experimental detection of such a weak feature would surely be extremely difficult. The calculated shift in frequency of the antisymmetric stretching mode induced by substitution of two ^{15}N atoms is 32.7 cm^{-1} for both linear and C_{2v} geometries (experimental results: 31.6 cm^{-1} in argon) [2]. These observations lead us to believe that the linearity of NUN is not established beyond all doubt from the experimental data currently available. Similar remarks have already been made for NUO^+ by Andrews and co-workers [25], though our results favour linearity in that case.

Matrix effects on vibrational wavenumbers have been studied for NUN and NUO. Data for both argon and neon matrices are available for these two cases [2]. We estimate the gas-phase vibrational wavenumber by supposing that the vibrational perturbation is proportional to the polarizability of the appropriate rare gas (1.65 \AA^3 for Ar and 0.4 \AA^3 for Ne). Since the stretching wavenumbers observed for NUN in Ar and Ne matrices

are 1051.0 and 1076.6 cm^{-1} , respectively, our extrapolated gas-phase value is 1083 cm^{-1} . The observed values for the higher-frequency mode of NUO in Ar and Ne matrices are 983.6 and 1004.9 cm^{-1} , leading to a gas-phase estimate of 1010 cm^{-1} . Since these estimates of the correction to be applied to data obtained in Ne matrices are similar for NUN and NUO (5 or 6 cm^{-1}), we decided to apply the same “correction” to the matrix data available for CUO and NUO^+ .

Anharmonic effects have been calculated as described above for UO_2^{2+} and CUO, and the resulting vibrational wavenumbers for states below about 3600 cm^{-1} are given in Tables 3 and 4. Although we do not claim that DFT is capable of establishing these effects with very high accuracy, we believe that it is quite sufficient to yield accuracies of a few cm^{-1} in these cases. Two significant results can be derived from these calculations. First, the anharmonic effects are relatively small in the uranium compounds for the medium IR region, less than 10 cm^{-1} , or less than 1% (the fact that these effects are relatively small supports our belief that DFT may be used to establish them to within a few cm^{-1} , since this is a relative accuracy of only some 30–50%). Second, they differ appreciably for the two molecules: 6.4 and 5.9 cm^{-1} for $\omega(\sigma_u)$ and $\omega(\sigma_g)$ for UO_2^{2+} , but 9.1 and 5.0 cm^{-1} for $\omega(\text{CU})$ and $\omega(\text{OU})$ for CUO. We assumed that the effects of vibrational anharmonicity in NUN are the

Table 4

Anharmonic wavenumbers calculated for the ground state of CUO: dominant contributions for the lowest transitions

Name	Calculated wavenumbers (cm^{-1})	Description	Name	Calculated wavenumbers (cm^{-1})	Description
$\nu_1(*)$	1122.9	0.98(100)			
$\nu_2(*)$	884.5	0.98(010)			
$\nu_3(*)$	88.8	0.99(001)			
$2\nu_3$	176.8	0.99(002)	$2\nu_2 + 4\nu_3$	2115.5	0.88(024) + 0.07(034)
$3\nu_3$	264.0	0.99(003)	$2\nu_1 + 3\nu_3$	2490.2	0.87(203)
$4\nu_3$	350.4	0.98(004)	$\nu_1 + \nu_2 + 4\nu_3$	2349.4	0.89(114)
$\nu_2 + \nu_3$	973.4	0.97(011)	$2\nu_2 + 5\nu_3$	2201.7	0.87(025) + 0.07(035)
$\nu_1 + \nu_3$	1209.2	0.98(101)	$2\nu_1 + 4\nu_3$	2573.4	0.84(204)
$\nu_2 + 2\nu_3$	1061.5	0.97(012)	$\nu_1 + \nu_2 + 5\nu_3$	2433.3	0.86(115)
$\nu_1 + 2\nu_3$	1295.6	0.98(102)	$3\nu_2$	2641.8	0.80(030) + 0.10(040)
$\nu_2 + 3\nu_3$	1148.7	0.97(013)	$2\nu_1 + 5\nu_3$	2655.9	0.81(205)
$\nu_1 + 3\nu_3$	1381.2	0.97(103)	$2\nu_1 + \nu_2$	3117.7	0.90(210)
$\nu_2 + 4\nu_3$	1234.9	0.96(014)	$3\nu_2 + \nu_3$	2731.0	0.82(031) + 0.11(041)
$\nu_1 + 4\nu_3$	1466.0	0.95(104)	$\nu_1 + 2\nu_2$	2884.0	0.90(120)
$\nu_2 + 5\nu_3$	1320.2	0.94(015)	$\nu_1 + 2\nu_2 + \nu_3$	2971.6	0.88(121)
$\nu_1 + 5\nu_3$	1550.0	0.97(105)	$3\nu_1$	3346.8	0.82(300) + 0.11(400)
$2\nu_2$	1765.0	0.93(020)	$3\nu_2 + 2\nu_3$	2819.2	0.84(032) + 0.09(042)
$\nu_1 + \nu_2$	2005.0	0.95(110)	$2\nu_1 + \nu_2 + \nu_3$	3204.5	0.89(211)
$2\nu_2 + \nu_3$	1854.0	0.92(021)	$\nu_1 + 2\nu_2 + 2\nu_3$	3058.3	0.86(122) + 0.07(132)
$2\nu_1$	2236.3	0.96(200)	$3\nu_2 + 3\nu_3$	2906.3	0.79(033) + 0.12(043)
$\nu_1 + \nu_2 + \nu_3$	2092.4	0.94(111)	$2\nu_1 + \nu_2 + 2\nu_3$	3292.6	0.89(212)
$2\nu_2 + 2\nu_3$	1942.2	0.91(022)	$2\nu_1 + \nu_2 + 3\nu_3$	3480.5	0.92(213)
$2\nu_1 + \nu_3$	2321.7	0.96(201)	$3\nu_2 + 4\nu_3$	2992.6	0.77(034) + 0.13(044)
$\nu_1 + \nu_2 + 2\nu_3$	2179.0	0.93(112)	$\nu_1 + 2\nu_2 + 3\nu_3$	3237.4	0.68(123) + 0.26(035)
$2\nu_2 + 3\nu_3$	2029.3	0.90(023)	$3\nu_2 + 5\nu_3$	3246.7	0.26(123) + 0.66(035)
$2\nu_1 + 2\nu_3$	2406.3	0.89(202)	$\nu_1 + 2\nu_2 + 5\nu_3$	3429.4	0.63(125) + 0.24(301)
$\nu_1 + \nu_2 + 3\nu_3$	2264.6	0.91(113)	$3\nu_1 + \nu_3$	3430.8	0.29(125) + 0.57(301)

Table 5
Quartic force fields calculated for CUO and UO_2^{2+} ^a

Force constant ^b	CUO	UO_2^{2+}
f_{RR}	7.807	10.474
$f_{Rr}/f_{RR'}$	-0.774	-0.290
f_{rr}	7.818	
$f_{\alpha\alpha}$	0.092	0.347
f_{RRR}	-27.684	-51.042
$f_{RRr}/f_{RRR'}$	4.517	-1.703
f_{Rrr}	-26.284	
f_{rrr}	4.356	
$f_{R\alpha\alpha}$	-0.544	-0.455
$f_{r\alpha\alpha}$	-0.133	
f_{RRRR}	42.935	436.49
$f_{RRRr}/f_{RRR'R'}$	-4.928	-64.86
$f_{RRrr}/f_{RRR'R'}$	83.640	147.01
f_{Rrrr}	-9.047	
f_{rrrr}	77.053	
$f_{RR\alpha\alpha}$	1.101	2.855
$f_{Rr\alpha\alpha}/f_{RR'\alpha\alpha}$	0.961	-1.825
$f_{r\alpha\alpha\alpha}$	-0.332	
$f_{\alpha\alpha\alpha\alpha}$	0.127	3.583

^a Units are $\text{aJ } \text{\AA}^{-m} \text{ rad}^{-n}$ for m stretching and n bending coordinate. B3LYP energies used; see text.

^b First entry is notation appropriate for CUO, second for UO_2^{2+} . R represents U–C and r is U–O in CUO.

same as those for UO_2^{2+} , and that those in NUO^+ and CUO are also identical. The data in the “corrected” experimental column of Table 1 have been treated accordingly. The quadratic, cubic and quartic force constants obtained for UO_2^{2+} and CUO are presented in Table 5.

4. Discussion

In Table 2, we compare the overall performance for vibrational wavenumbers of the different DFT versions that we have tested. The CASPT2 results of Gagliardi and Roos [13] are also reported, for purposes of comparison. For the five stretching modes in our sample, corrected both for matrix and anharmonicity effects as described above, we present first the average error without regard to sign, second the average error when cancellation is permitted between positive and negative errors, and third the maximum error found in our sample. Although the sample is still very limited in size, we believe that it is large enough for several general conclusions to be drawn.

We note first that the “corrected” experimental values are subject to uncertainties of perhaps 8–10 cm^{-1} . This means that it is futile to attempt to analyze small differences too finely. But even with this limitation, it is clear that the hybrid versions of DFT *systematically overestimate* the vibrational stretching frequencies. The most telling point in this context is that the unsigned and signed errors (columns 2 and 3) are identical, i.e., there is *no* case of a calculated frequency being too low. Of the

different hybrid versions, B3LYP is the least bad and PBE0 the worst.

Next we note that BLYP (GGA type) *systematically underestimates* the vibrational wavenumbers, its average error being indistinguishable in magnitude from that of its hybrid cousin B3LYP. However, the three other GGA versions BPW91, PW91 and PBE all perform very well, with average errors that are smaller than the estimated uncertainties in the corrected experimental data. Even the largest individual error is only 24 cm^{-1} , or 2.3% for BPW91 and PW91, though PBE is a little less successful as its largest individual error is 40 cm^{-1} . It is salutary to note that the LDA, the least sophisticated of those in our selection, performs better than *all* the hybrid versions, though less well than the GGA versions already considered. The generally good performance of the LDA for systems containing very heavy atoms has already been noted [26].

CASPT2 calculations are also accurate, but only with much larger basis sets than those used for the DFT results in Table 1; an average (signed) error of -18 cm^{-1} is obtained with the “large” ANO basis on C, N and O when g-type functions are included in the U basis, and the results are systematically too low, as the signed and unsigned errors are equal in magnitude. However, this result is not strictly comparable with the others; it is based on only three vibrational modes, since no CASPT2 calculations were undertaken on NUO^+ with this basis. When the g-type functions are omitted, the performance becomes substantially poorer than that offered by the three GGA versions already highlighted; the average signed error is now -41 cm^{-1} , with a largest error of -58 cm^{-1} . (If calculated for the three modes for which the basis including g-type functions was used, the average signed error is marginally smaller, at -38 cm^{-1} , suggesting that the value of -18 cm^{-1} obtained with the biggest basis is representative of the result that the full sample of vibrational modes would yield.) The sensitivity of CASPT2 results to the size of the basis is worth noting; the addition of f-type functions to the C, N or O bases produces changes of -33 , -53 , -81 , $+72$ and -9 cm^{-1} , for NUN, NUO^+ (two modes) and CUO (two modes), respectively. These changes are both substantial *and* highly variable from one molecule to another. They are particularly puzzling when the geometrical changes due to these basis extensions are also considered; the bonds are consistently shortened by about 0.015 \AA for all three molecules, yet most of the vibrational frequencies are *decreased* by the addition of f-type functions to C, N and O (see below for further discussion of bond length/vibrational frequency relationships). The addition of g-type functions to the U basis gives changes of $+41$, $+8$ and $+11 \text{ cm}^{-1}$ for NUN and CUO (two modes), respectively. Since the performance of the CASPT2 method is not better than that of the BPW91, PW91 or PBE versions of DFT, since it is far more

computationally demanding and needs very careful attention to the size of basis to ensure that converged results are obtained, we believe that its superiority as a method for calculation of vibrational frequencies has not been established, at least for closed-shell molecules of the type considered here. Some experimental IR data are also available for open-shell systems derived from the uranyl dication by successive addition of electrons; the antisymmetric stretching mode is found in Ne matrices at 980, 914 and 857 cm^{-1} , for UO_2^+ , UO_2 and UO_2^- , respectively [8]. We have already reported that the B3LYP predictions of 1010, 931 and 874 cm^{-1} , respectively, are highly satisfactory [8]. Yet PW91 performs uncannily well, as it yields predictions of 980, 909 and 858 cm^{-1} , i.e., errors compared to the matrix data of only <1, 5 and <1 cm^{-1} . PW91 also gives remarkably accurate predictions for another open-shell molecule, neutral NUO; its predictions of 1012 and 832 cm^{-1} are extremely close to the observed Ne-matrix data (1005 and 834 cm^{-1}), and significantly better than those yielded by B3LYP (1047 and 850 cm^{-1}). While it is too early to conclude that the PW91 version of DFT will be universally successful for the prediction of vibrational frequencies, as the effects of spin–orbit coupling have yet to be incorporated (work along these lines is currently in progress), these few examples suggest that its potential for open-shell compounds is very promising, and that it should be preferred to B3LYP for actinide-containing compounds.

When we consider the results for different molecules obtained at a given level of theory, it is striking that *almost every* DFT version performs least well for CUO, where the higher frequency stretching mode is particularly prone to errors; BLYP is the only version of DFT to underestimate this mode. In an effort to discover why CUO should be a much more challenging molecule than the others, we performed some CASSCF and CASPT2 calculations at the CASSCF geometries [27], using the same basis sets as Gagliardi and Roos [13]. The coefficients of the HF reference configuration in the CASSCF calculations are 0.93, 0.93 and 0.94 for UO_2^+ , NUN and CUO, respectively, while the CASSCF reference weights in the CASPT2 calculations are 0.89 for UO_2^+ , 0.85 for NUN and 0.84 for CUO. Taken together, these data do not readily explain why CUO is apparently the most difficult molecule in our sample for the hybrid versions of DFT. Searching for other molecular properties that appear to be correlated with the degree of success in the calculation of vibrational frequencies, we note, empirically, the utility of the HOMO–LUMO separation as an indicator. For UO_2^+ , NUO^+ , NUN and CUO, these separations are 0.643, 0.476, 0.358 and 0.313 au, respectively, at the SCF level, or 0.193, 0.140, 0.155 and only 0.090 au with B3LYP. It is clear that the accuracy of the B3LYP (and other hybrid) frequency predictions declines as the HOMO–LUMO gap becomes smaller,

but this empirical observation provides little insight. Moreover, we note that the HOMO–LUMO gap is systematically smaller with GGA functionals than with hybrid DFT versions, to the point of becoming *negative* for singlet CUO (i.e., the aufbau principle is not respected), yet most of the GGA versions are very successful for *all* the molecules in our sample. The quantity known as the “T1 diagnostic” [28] is another potential indicator. The values obtained at the optimum CCSD geometries are 0.032, 0.031, 0.033 and 0.047 for UO_2^+ , NUO^+ , NUN and CUO, respectively. These data imply an appreciably greater multireference character for CUO than for the other XUY molecules, and therefore that prediction of vibrational frequencies will indeed be more difficult for CUO than for the other cases. Yet it is not clear why the CAS method, in contrast to the T1 diagnostic, implies a similar multireference character for all our molecules, nor why the GGA versions such as PW91 are apparently capable of treating correctly molecules whose multireference character is substantial (the creators of the T1 diagnostic suggest that the (single-reference) CCSD method starts to become unsuitable for values above about 0.02). We note that we are not the first to observe that hybrid versions of DFT can have shortcomings in actinide chemistry; Vetere et al. [29] have studied metal–ligand interactions in U(III) complexes, and have reported much better performance with GGA than with hybrid functionals.

When considering the performance of various theoretical methods for the prediction of vibrational spectra, it is important to consider predicted intensities as well as wavenumbers, even if precise measurements of the former are much more difficult than for the latter. Some experimental data are available; for both UNO^+ and CUO, the two stretching modes have the same relative intensities, with uncertainties of about 30% and 10%, respectively [30]. For UNO^+ , the calculated intensity of the higher-frequency stretching mode is 50%, 70%, 44%, 44%, 27% or 24% higher than that of the lower-frequency mode, using the LDA, BLYP, BPW91, PW91, B3LYP and B3PW91 versions of DFT, respectively. It is clear that the calculated intensities are more variable than the frequencies, even on a relative basis; the hybrid versions of DFT appear to have some advantage here, though unfortunately the experimental uncertainties are quite large. For CUO, the higher-frequency mode is calculated to be less intense than the lower, by 12%, 19%, 1%, 7%, 20% and 10%, in the same order as above. No clear advantage is apparent here for any type of functional, and all perform with at least semi-quantitative accuracy. More precise experimental data will be necessary if this aspect of the performance of DFT is to be assessed more strictly. At the CASPT2 level of theory, the relative intensities (in the same sense as the results presented above) are 76% higher for UNO^+ and 13%

lower for CUO [13]; these are not greatly different from the DFT values.

The electronic structure of CUO turns out to be remarkably complex and interesting. Andrews and co-workers have reported that an excited triplet state ($^3\Phi$) lies only 6.5 kJ/mol above the electronic ground state ($^1\Sigma^+$), if spin–orbit effects are neglected [3a]. These two states have quite different geometries, the U–C bond being as much as 0.1 Å longer in the triplet state, so the vibrational frequencies predicted for these two states are also quite different and capable of distinguishing between them. In our DFT calculations, the triplet state is in fact a little more stable than the singlet, by 21 or 26 kJ/mol, at the B3LYP or PW91 levels of theory. However, when CCSD theory is used with a basis containing g-type functions on U, the singlet is found to be more stable by 37 kJ/mol (the optimized CCSD bond lengths of singlet CUO are U–O 1.778 Å and U–C 1.752 Å, i.e., similar to the DFT results), and the CCSD(T) method at the CCSD geometry increases the relative stability of the singlet a little, to 44 kJ/mol. But is it realistic to ignore spin–orbit coupling effects, which will surely be larger for a triplet state than a singlet? We draw attention to a very recent publication by Roos et al. [31] they have studied spin–orbit effects in CUO, and they report that the ground state is of Φ -type, with $\Omega = 2$. We note, however, that the vibrational spectra predicted by DFT for singlet CUO without any treatment of spin–orbit effects are very close to the data observed in Ne matrices, whereas the experimental results in Ar matrices match theoretical predictions for the triplet state reasonably well [3a]. It is clear that the electronic structure of CUO still deserves further attention. The work by Andrews and co-workers [32] on the incipient bonds formed between noble-gas atoms such as Ne or Ar and CUO is important in this context.

Analysis of the data in Tables 3 and 4 show that the harmonic and combination bands of UO_2^{2+} and CUO are generally uncoupled. A dominant contribution is present in each case, leading to an unambiguous description of the vibrational motions. The weak influence of the anharmonic contribution should be noted for all bands, for both UO_2^{2+} and CUO. More precisely, the anharmonicity is generally small and does not exceed 1% (about 10 cm^{-1}) or 2% for the stretching or bending modes, respectively. In the case of UO_2^{2+} , the cubic and quartic force constants show a significant influence of the coefficients involving the U=O stretching mode, particularly for ϕ_{111} and ϕ_{1111} (180 and 31 cm^{-1}) and its coupling ϕ_{122} and ϕ_{1122} (177 and 23 cm^{-1}), but no resonance could be determined. Similar behaviour is observed for CUO. Two dominant anharmonic constants appear in this case: ϕ_{111} (289 cm^{-1}) and ϕ_{222} (196 cm^{-1}). The weak anharmonic coupling between the two stretching and the bending modes cannot induce a strong change in our calculations. All the cubic coupling

constants are in the range of 10–80 cm^{-1} , so their maximal diagonal contribution is only 5 cm^{-1} in the diagonalization scheme. This behaviour is new when compared with uranyl, but does not drastically change the conclusions. We are thus not able to predict any particular resonance for these two systems.

Individual valence-type force constants for UO_2^{2+} and CUO are presented in Table 5. We call attention to the *negative* value of the bond–bond interaction force constant for both systems. A negative interaction force constant is most unusual (in CO_2 , the analogous force constant is +1.26 aJ Å^{-2} [33]); it implies a cooperative effect between the two bonds, since a decrease in one bond length will induce a shortening in the other. This observation deserves further attention.

We return to the data in Table 1 concerning optimized U–X bond distances. As no experimental results are available for these quantities, it is not possible to check the accuracy of the calculated values in any direct way. However, the importance of the choice of reference geometry in the calculation of force constants was established in the early days of computational quantum chemistry [34]. It is clear from Table 1 that for a given molecule, there is a strong inverse correlation between the optimized bond length and the calculated stretching frequencies. To emphasize this point, we plot the calculated U=O bond stretching harmonic force constant for the uranyl ion in Fig. 1 as a function of bond length. Both HF and B3LYP results are presented; the two smooth curves join the points obtained at different distances. The two curves are almost superposable, showing that the force constant in fact depends essentially only on the U=O distance, the direct influence of correlation being very small. (But as correlation effects lengthen the bonds appreciably, by some 0.06 Å, the indirect effect of correlation on the force constant is significant.) U=O force constants obtained for UO_2^{2+} , CUO and NUO^+ with other functionals are also plotted in Fig. 1 as individual points. In the uranyl ion case, all the points are essentially on the two curves, confirming that the calculated U=O force constant depends only on the U=O distance, whatever the method used. For CUO and NUO^+ , the points are not far from the full curves, and they also show an approximately exponential variation with bond distance. We could also include other calculated U=O force constants for complexes of the uranyl ion containing ligands such as H_2O or F^- ; these points would also lie very close to the full curves, but Fig. 1 would then become too cluttered to be read easily. Since the interaction force constant linking the two U=O bonds in the uranyl ion is very small compared to the stretching force constant (see Table 5), the vibrational frequencies depend essentially only on the latter. The vibrational frequencies, which can readily be measured for uranyl complexes in solution or the solid state, therefore depend directly on the U=O bond distance. Moreover, they are a sensitive probe of

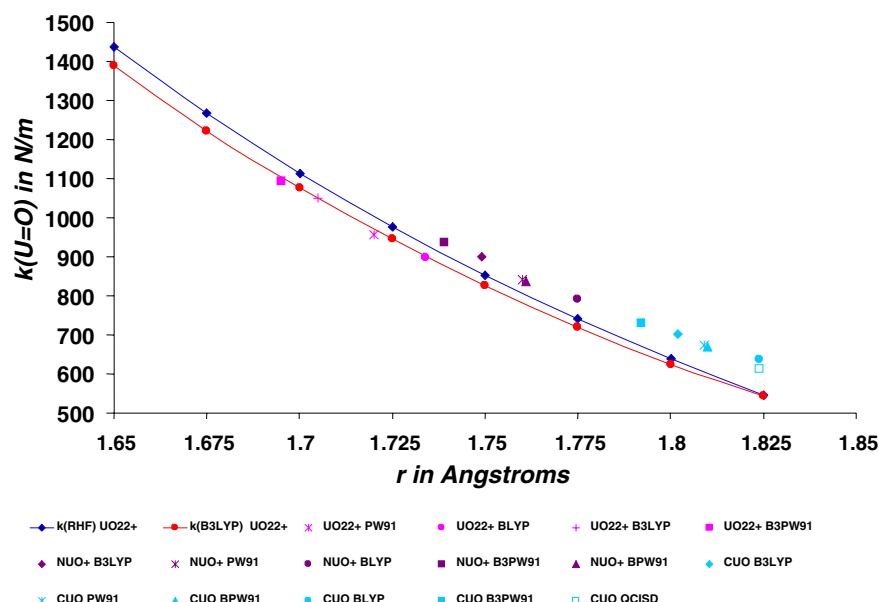


Fig. 1. Harmonic U=O force constant as a function of U=O distance (uranyl ion and uranium triatomic molecules).

that distance, given the slope of the curves in Fig. 1. Empirical equations have indeed been proposed linking vibrational frequencies to U=O bond lengths [35], but to the best of our knowledge, no theoretical justification has yet been proposed. Badger's rule may be expressed as

$$r(\text{U=O}) = [H/(k^{1/3})] + L,$$

if the U=O distance r is expressed in Å and the force constant k in aJ Å^{-2} , the appropriate numerical values for the constants are $H = 1.08$ (a universal parameter) and $L = 1.21$ [36]. An expression of this type can readily be fit to our B3LYP data for the uranyl dication shown in figure; the correlation coefficient is 0.996, with $H = 1.138$ and $L = 1.183$ (units are Å). Since the agreement with the empirical values is quite satisfactory, we deduce that our calculated curve is reasonably reliable.

5. Conclusions

We have shown that some versions of DFT give very successful predictions of the vibrational frequencies of the closed-shell molecules NUN, NUO⁺ and CUO. GGA functionals are more successful than are hybrid versions, despite the presence of empirical parameters in the latter. The PW91, BPW91 and PBE versions of DFT are at least as accurate as CASPT2, and much more readily applicable to larger molecules. It remains to be seen whether they will also perform well for open-shell systems, where spin-orbit effects may be non-negligible, though the first indications for UO₂⁺, UO₂, UO₂⁻ and NUO are encouraging. Calculated IR intensities are in at least semi-quantitative agreement with experiment, though the available data are not yet very precise. CUO causes far

more serious problems than do the other molecules for the calculation of vibrational frequencies; we have not been able to find a completely satisfactory explanation of this observation. We suggest that the vibrational data now becoming available for actinide-containing molecules could *and should* be used to improve the empirical parameters incorporated in hybrid versions of DFT, since the current values of these parameters, which are intended to have universal applicability, are clearly inappropriate for the actinides. For both UO₂²⁺ and CUO, the influence of anharmonicity on the vibrational frequencies has been calculated using DFT and shown to be rather small. Since we have shown that the U=O force constant in UO₂²⁺ depends only on the U=O distance, we infer that vibrational spectra can be used to estimate U=O distances quickly, when these are not directly available, with reasonable precision and reliability.

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