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Theoretical study of the electronic spectra of neutral and cationic NpO and NpO₂

Attila Kovács¹ and Ivan Infante²
¹European Commission, Joint Research Centre, Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany
²Department of Theoretical Chemistry, Faculty of Sciences, Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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The electronic spectra of neutral NpO and NpO₂ as well as of their mono- (NpO⁺, NpO₂⁺) and dications (NpO⁺², NpO₂⁺²) were studied using multiconfigurational relativistic quantum chemical calculations at the complete active space self-consistent field/CASPT2 level of theory taking into account spin-orbit coupling. The active space included 16 orbitals: all the 7s, 6d, and 5f orbitals of neptunium together with selected orbitals of oxygen. The vertical excitation energies on the ground state geometries have been computed up to ca. 35 000 cm⁻¹. The gas-phase electronic spectra were evaluated on the basis of the computed Einstein coefficients at 298 K and 3000 K. The computed vertical transition energies show good agreement with previous condensed-phase results on NpO⁺ and NpO₂⁺². © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4928588]

I. INTRODUCTION

Neptunium oxides are present in notable amount in spent nuclear fuel, for which several reprocessing and recycling technologies have been developed, including oxide-based transmutation fuels.¹-⁶ However, these technologies can gain from optimization of the conditions, requiring an accurate knowledge of the molecular properties of all actinide compounds present in the fuel.

In contrast to the detailed experimental description of the solid neptunium oxides,⁷ their molecular properties are less explored. To obtain them requires difficult and expensive gas-phase experiments which were performed hitherto for the ionization energies (NpO⁺⁶-¹⁰ and NpO₂⁺⁶-¹⁰) and dissociation energies of both the neutral oxides and their cations.¹⁰,¹¹ Structural and vibrational data on the NpO and NpO₂ molecules are available from quantum chemical calculations only.¹²,¹³

Experimental studies of the electronic structure were performed for the ions NpO₂⁺ and NpO₂⁺² and only in condensed phases. Early absorption spectra of Np oxides (and also other actinide compounds) were reviewed in Ref. 14 and 15. Both ions were investigated by UV/VIS absorption spectroscopy in aqueous acidic solutions,¹⁶-¹⁸ accompanied by separate studies on NpO₂⁺¹⁹ and on NpO₂⁺².²⁰ The absorption spectrum of NpO₂⁺ was also recorded in the form doped into Cs₂UO₂Cl₄ and CsUO₂(NO₃)₂ crystals.²¹-²⁵ These latter spectra were similar to the solution ones implying that the transition energies are not much affected by the environment. The ground electronic states could be well determined on the basis of the above experiments: they are the ⁵H₄₄ ground state for NpO₂⁺ and the ⁴D₅/₂u state for NpO₂⁺².²³,²⁴,²⁶

The electronic spectra of the solutions were first assigned using semi-empirical ligand-field theory (NpO₂⁺²⁷ and NpO₂⁺²⁸) and were revised later by quantum chemical calculations.¹⁹,²⁵-²⁹,³⁵ Matsika et al.¹⁹,²⁵,²⁹ used configuration interaction methods in conjunction with relativistic effective core potentials that incorporate also spin-orbit coupling (SO-MRCI). In one of these studies,¹⁹ coordination models with five explicit coordinating water molecules and chloride ions, respectively, were tested. Infante et al.³⁰ used for the free ions the more advanced intermediate Hamiltonian Fock-space coupled-cluster (IHFSCC) method in conjunction with the Dirac-Coulomb Hamiltonian which accounted for relativistic effects including spin-orbit coupling as well. Recently, Danilo et al. applied SO-CASPT2 and SO-MRCI calculations using a small active space for modelling the free and hydrated NpO₂⁺ (the latter as [NpO₂(H₂O)₄]²⁺) ions.³² The ground and the few lowest-energy excited states of NpO₂⁺² and of the NpO₂Cl₄²⁻ complex ion (model for the Cs₂NpO₂Cl₄ solid-phase spectra) were investigated by Gomes et al. using IHFSCC.³¹ They considered further environmental effects on NpO₂Cl₄²⁻ by means of density functional theory (DFT) embedding. The hitherto most complete assessment of the electronic spectrum of Cs₂NpO₂Cl₄ at an adequate level of theory was performed by Su et al.³³ who calculated both the vertical and adiabatic transitions of NpO₂⁺² and NpO₂Cl₄²⁻ up to 21 000 cm⁻¹ using the SO-RASPT2 method. The electronic structure and magnetic properties of NpO₂⁺² and a few complexes: NpO₂Cl₄²⁻, [NpO₂(NO₃)₄]²⁻, and [NpO₂(CO₃)₃]⁴⁻ were studied by Gendron et al.³⁴,³⁵ using a combination of theoretical (among them SO-CASPT2) methods. The studies included a detailed analysis of SO coupling involving the first four electronic states of the given molecules.

In other recent studies, only the ground-state electronic structure and molecular properties were investigated: Liao et al. computed NpO₂ and NpO₂⁺² using relativistic DFT calculations.³⁷ They reported the electronic ground states of
NpO\textsubscript{2} and NpO\textsubscript{2}\textsuperscript{2+} (that of NpO\textsubscript{2} erroneously as \(4\Sigma_g^\text{e}\)) as well as the first and second ionization energies of NpO\textsubscript{2}. Several computational studies were performed on neutral and ionic neptunium mono- and dioxides at SO-CASPT2 and various DFT levels resulting in theoretical ionization energies, vibrational frequencies, and dissociation energies. The hydration and oxidation reactions of NpO\textsubscript{2}\textsuperscript{2+} in the gaseous phase were studied by DFT assisting electrospray experiments, while NpO\textsubscript{2}\textsuperscript{2+} served as model compound in a benchmark study of two-component relativistic DFT methods.

The goal of the present study is the systematic evaluation of the gas-phase electronic spectra of the neutral and ionic NpO and NpO\textsubscript{2} species by means of multireference relativistic \textit{ab initio} calculations on the basis of our previous studies on the electronic ground states of these species. Other important results from the present calculations are the energies of the excited states, required for a reliable evaluation of the thermodynamic functions of the gaseous oxides. Such thermodynamic data are utilized in developing safety procedures in nuclear industry.

II. COMPUTATIONAL DETAILS

The calculations were performed using the software MOLCAS 7.4. The complete active space self-consistent field (CASSCF) method was used to generate molecular orbitals and reference functions for subsequent multiconfigurational second-order perturbation theory calculations of the dynamic correlation energy (CASPT2). In the case of the monoxides, the active space consisted of 7s, 6d, and 5f orbitals of the actinide atoms as well as of the 2p orbitals of oxygen. This means 16 orbitals occupied by 11, 10, and 9 electrons for NpO, NpO\textsuperscript{+}, and NpO\textsuperscript{2+}, respectively. An analogous construction of the active space of the dioxides would result in 19 orbitals occupied by 13-15 electrons in the studied dioxides species, which is nowadays computationally unfeasible due to the large amount of configuration state functions. Therefore, we used a truncated space of 14 orbitals, omitting the two lowest \(\pi_g^\text{e}\) bonding and the corresponding antibonding orbitals and one \(\pi_g^*\) antibonding orbital. This active space included 11, 10, and 9 electrons for NpO\textsubscript{2}, NpO\textsubscript{2}\textsuperscript{+}, and NpO\textsubscript{2}\textsuperscript{2+}, respectively. We neglected the Np 7p orbitals due to their relatively high energy with respect to the 5f, 6d, and 7s orbitals, which makes them less important in low-energy excitations. Accordingly, previous studies of the electronic spectra of NpO\textsubscript{2}\textsuperscript{+} and NpO\textsubscript{2}\textsuperscript{2+} did not find any significant excitations to Np 7p orbitals.

As MOLCAS can handle only Abelian point groups, the point groups of the target molecules (D\sub{oh} and C\sub{no}) could not be applied. In order to be consistent for the mono- and dioxides, we used the C\sub{2v} approach in our calculations. This might lead to symmetry breaking effects resulting in some cases to spurious orbital mixing. After investigation of the trial orbitals, the CLEAnup keyword of MOLCAS was applied to minimize as much as possible this shortcoming.

The ground state molecular geometries of the title Np oxides reported in Ref. 12 were applied in the present study. The vertical excited electronic states were explored by multiconfigurational state-averaged calculations using up to 30 roots for a given spin multiplicity and symmetry. In addition to the ground-state spin multiplicity \(4, 3, 2, 6, 5, 4\) for NpO\textsubscript{2}, NpO\textsuperscript{2+}, NpO\textsuperscript{2+}, NpO\textsuperscript{+}, NpO\textsuperscript{0}, and NpO\textsuperscript{2+}, respectively, generally the two neighbouring (lower and higher) ones were considered too. For details, see the supplementary material.

All electron basis sets of atomic natural orbital type, developed for relativistic calculations (ANO-RCC) with the Douglas-Kroll-Hess Hamiltonian, which allows CASSCF wave functions for different electronic states to interact under the influence of a spin-orbit Hamiltonian. Dynamic electron correlation is taken into account using the CASPT2 energies as spin-orbit free (SF) energies in the spin-orbit Hamiltonian (SO-CASPT2). The above described multireference methods and the ANO-RCC basis set were successfully applied in a number of studies on actinide-containing systems.

III. RESULTS AND DISCUSSION

A. NpO\textsubscript{2}, NpO\textsubscript{2}\textsuperscript{+}, and NpO\textsubscript{2}\textsuperscript{2+}

Literature information on these molecules involves the ground electronic states of all three species and the electronic spectra of the NpO\textsubscript{2}\textsuperscript{+} and NpO\textsubscript{2}\textsuperscript{2+} ions. We computed the excited electronic states up to ca. 35 000 cm\textsuperscript{-1} using the SO-CASPT2 method. As these states were obtained on the ground state geometries, the computations provided us the vertical excitation energies. On the basis of the excited states and the computed Einstein coefficients, we could model the gas-phase electronic spectra. The spectra were calculated at two temperatures, 298 K (to be compared with reported solution and solid-phase spectra at room temperature) and 3000 K (modeling high-temperature gas-phase studies). The calculated electronic spectra are presented in Figure 1. In Tables I–III, the most intense transitions for NpO\textsubscript{2}, NpO\textsuperscript{2+}, and NpO\textsuperscript{2+}, respectively, are compiled and characterized. The characterization is based on the major population differences...
between the donor and acceptor SO states. The full lists of the obtained SF and SO states are given in the supplementary material.

In the spectra at 298 K, only excitations from the ground states appear with considerable intensity. Due to the population of low-lying excited states at high temperatures, the spectra simulated for 3000 K contain several additional lines compared to those at 298 K.

In the computed spectrum of NpO$_2$ (Figure 1), the two major peaks at 15 101 and 27 398 cm$^{-1}$ correspond to transitions 7s $\rightarrow$ 5f$\pi$ and 5f$_{\delta}$ $\rightarrow$ 6d$_{\delta}$, respectively. At 3000 K, two another major bands join them at 23 752 and 30 024 cm$^{-1}$ corresponding to transitions from the first excited state. We note that the main difference between the ground and first excited states of NpO$_2$ is the inverted spin of the 7s electron. Thus, the former band represents a 7s$^\beta$ $\rightarrow$ 5f$_{\phi}^\beta$ transition.

FIG. 1. Simulated gas-phase absorption electronic spectra of NpO$_2$, NpO$_2^+$, and NpO$_2^{2+}$. 
### TABLE I. Significant computed electronic transitions (cm⁻¹) of NpO₂⁺.

| Intensity | Energy | 298 K | 3000 K | Einstein | From | To | Main orbitals involved |
|-----------|--------|-------|--------|----------|------|---|------------------------|
| 8 175     | 6      | 6     | 376 108 | 1(3.5)_g | 11(4.5)_u | 7s→5f₈  |
| 11 632    | 6      |       | 565 672 | 2(4.5)_g | 24(5.5)_u | 7δ→5f₈  |
| 13 279    | 7      |       | 727 434 | 2(4.5)_g | 28(3.5)_u | 7δ→5f₈  |
| 13 861    | 10     |       | 1 008 360 | 2(4.5)_g | 29(3.5)_u | 7δ→5f₈  |
| 15 101    | 20     | 20    | 1 325 410 | 1(3.5)_g | 31(2.5)_u | 7s→5f₈  |
| 16 235    | 5      | 5     | 332 063 | 1(3.5)_g | 35(2.5)_u | 7s→5f₈  |
| 17 725    | 5      | 5     | 302 602 | 1(3.5)_g | 40(2.5)_u | 7s→5f₈  |
| 19 182    | 3      |       | 2 760 353 | 5(4.5)_g | 75(5.5)_u | 7δ→5f₈  |
| 23 753    | 1      | 57    | 5 838 593 | 2(4.5)_g | 75(5.5)_u | 7δ→5f₈  |
| 27 398    | 100    | 100   | 6 744 513 | 1(3.5)_g | 84(3.5)_u | 5f₈→6d₈  |
| 30 024    | 31     |       | 3 196 690 | 2(4.5)_g | 97(4.5)_u | 7δ5f₈→7δ6d₈ |
| 31 800    | 8      |       | 8 099 030 | 2(4.5)_g | 103(5.5)_u | 7δ5f₈→5f₈5f₈  |

aThe energies of transitions are given in cm⁻¹, the relative intensities in % (using a threshold of 1%), and the Einstein coefficients in a.u.
bThe spin-orbit states defining the transitions; Ω values with parity in parentheses; for other details of the states, see the supplementary material STables 1 and 2.²⁶

### TABLE II. Significant computed electronic transitions (cm⁻¹) of NpO₂⁺.

| Intensity | Energy | 298 K | 3000 K | Einstein | From | To | Main orbitals involved |
|-----------|--------|-------|--------|----------|------|---|------------------------|
| 15 119    | 34     |       | 247 175 | 2(0.3)   | 13(0.3) | 5f₄, 2p₆→5f₈, 5f₈  |
| 16 011    | 57     | 57    | 90 713  | 1(4.8)   | 11(4.8) | 5f₈→5f₄, 5f₄, 2p₆  |
| 19 510    | 100    | 100   | 79 499 | 1(4.8)   | 15(4.8) | 5f₈→5f₄, 2p₆  |
| 23 877    | 58     |       | 207 982 | 2(0.3)   | 26(4.8) | 5f₈→5f₄, 2p₆  |
| 24 911    | 18     | 18    | 14 573  | 1(4.8)   | 24(4.8) | 5f₈→5f₄, 2p₆  |
| 25 400    | 20     | 20    | 31 960  | 1(4.8)   | 25(4.8) | 5f₈→5f₄, 2p₆  |
| 29 333    | 38     | 38    | 60 100  | 1(4.8)   | 33(4.8) | 5f₈→5f₄, 2p₆  |
| 29 822    | 41     | 41    | 32 622  | 1(4.8)   | 35(4.8) | 5f₈→5f₄, 2p₆  |
| 34 697    | 35     |       | 125 931 | 2(0.3)   | 46(4.8) | 5f₈→5f₄, 2p₆  |

aThe energies of transitions are given in cm⁻¹, the relative intensities in % (using a threshold of 1%), and the Einstein coefficients in a.u.
bThe spin-orbit states defining the transitions; Ω values with parity in parentheses; for other details of the states, see the supplementary material STables 3 and 4.²⁶

### TABLE III. Significant computed electronic transitions (cm⁻¹) of NpO₂⁺.

| Intensity | Energy | 298 K | 3000 K | Einstein | From | To | Main orbitals involved |
|-----------|--------|-------|--------|----------|------|---|------------------------|
| 13 806    | 4      |       | 2 729 959 | 6(4.5)_u | 20(4.5)_u | 5f₈→5f₈, 5f₄, 2p₆  |
| 14 642    | 54     |       | 7 372 243 | 5(3.5)_u | 17(3.5)_u | 5f₈→2p₄  |
| 15 892    | 9      |       | 6 490 881 | 7(0.5)_u | 24(0.5)_u | 5f₄, 2p₄→2p₆, 5f₈  |
| 16 018    | 4      |       | 6 892 856 | 8(1.5)_u | 31(1.5)_u | 5f₄, 2p₄→2p₆, 5f₄  |
| 16 688    | 6      |       | 3 915 076 | 6(4.5)_u | 27(3.5)_u | 5f₄→2p₄  |
| 28 747    | 100    | 100   | 159 422 | 12(2.5)_u | 25(3.5)_u | 5f₄, 2p₄→5f₄  |
| 29 302    | 10     | 10    | 16 239  | 12(2.5)_u | 27(3.5)_u | 5f₄, 2p₄→5f₄  |
| 30 288    | 44     | 44    | 69 948  | 12(2.5)_u | 28(3.5)_u | 5f₄, 2p₄→5f₄, 5f₈  |
| 32 959    | 26     | 26    | 42 144  | 12(2.5)_u | 34(2.5)_u | 5f₄, 2p₄→5f₄  |

aThe energies of transitions are given in cm⁻¹, the relative intensities in % (using a threshold of 1%), and the Einstein coefficients in a.u.
bThe spin-orbit states defining the transitions; Ω values with parity in parentheses; for other details of the states, see the supplementary material STables 5 and 6.²⁶
cβ means the inverted spin.
(where $\beta$ means the inverted spin), while the second, higher-energy, band corresponds to the double transition $7s^25f_{\beta} \rightarrow 7s6d_{\delta\beta}$. Other significant, but less intense transitions result in $7s \rightarrow 5f_{\alpha}$ (at 8175 cm$^{-1}$), some $7s^3 \rightarrow 5f_{\beta}$ and $7s \rightarrow 5f_{6s/6p}$ ones below and above 15000 cm$^{-1}$, respectively (cf. Table I). Double transitions appear characteristically above 30 000 cm$^{-1}$.

In the ground and the studied excited states of NpO$_2^+$, the Np 7$s$ orbital is not populated and the doubly occupied 5$f$ seems to be very stable; thus, the electronic transitions correspond essentially to population transfer mostly from orbitals having major 5$f_{\alpha}$ and 5$f_{\delta}$ contributions to ones having major 5$f_{\beta}$ contributions (cf. Table II). These originally electric dipole forbidden $f \rightarrow f$ transitions may become possible because the affected states contain minor contributions from 2$p$ orbitals of oxygen.

The room-temperature computed spectrum of NpO$_2^+$ shows four intense transitions (Figure 1), those at 16 011 cm$^{-1}$ (5$f_{\alpha} \rightarrow 5f_{\delta}$, 5$f_{\beta}$, 2$p_{\alpha}$), 19 510 cm$^{-1}$ (5$f_{\delta} \rightarrow 5f_{\alpha}$, 2$p_{\beta}$), 29 333 cm$^{-1}$ (5$f_{\alpha} \rightarrow 5f_{\sigma}$, 2$p_{\beta}$), and 29 822 cm$^{-1}$ (5$f_{\delta} \rightarrow 5f_{\tau}$, 2$p_{\beta}$). Due to the notable population of the low-lying excited states at 3000 K, the latter spectrum contains several intense transitions between 15 000 and 35 000 cm$^{-1}$. The main ones correspond to excitations from the ground and the first two excited states. Transitions accompanied with spin inversion appear at very high energy (e.g., the one at 34 697 cm$^{-1}$).

We note that the Einstein coefficients (and accordingly the expected absolute intensities in the spectrum) of NpO$_2^+$ are generally smaller by one order of magnitude than those of neutral NpO$_2$. This is due to the parity character of the states involved in the transitions. In the case of NpO$_2$, all the donor states in Table I have gerade ($g$) and the acceptor states ungerade ($u$) parity satisfying the Laporte rule. In contrast, in NpO$_2^+$, all the states have a dominant gerade character. According to the Laporte selection rule, electronic transitions that conserve parity are forbidden. In the case of NpO$_2^+$, the minor mixing of ungerade 2$p$ components in the SO states makes electronic transitions though possible, but with low probability. The case is similar for NpO$_2^{2+}$, where all the states have a dominant gerade character (cf. Table III).

Due to the decreased number of non-bonded valence electrons in NpO$_2^{2+}$, its electronic spectra (Figure 1) are poor in signals. There are three intense transitions at 298 K, while an additional one at 3000 K. Several lower-energy transitions (below 20 000 cm$^{-1}$) involve the excitation of a 5$f_{\sigma}$ electron to an anti-bonding (2$p$, 5$f$) orbital. The higher-energy transitions involve excitations of (mostly) a 5$f_{\delta}$ electron to another 5$f$ orbital, but some double excitations appear also here.

Having reliable gas-phase electronic transition energies of the neutral and ionic NpO$_2$ species, it can be interesting to see how they compare to previous experimental and theoretical investigations of the condensed-phase spectra of NpO$_2^+$ and NpO$_2^{2+}$. Due to the environment influencing considerably the spectral intensities in solutions and solids, our Einstein coefficients computed for the isolated molecules may not be suited for comparison. In contrast, the transition energies suffer less from the environment. Therefore, our assessments are done on the basis of the computed SO-CASPT2 energies and character ($\Omega$ value) of the excited states.

Selected experimental and theoretical results of NpO$_2^+$ are compiled in Table IV. The most recent study by Danilo et al. used SO-CASPT2 but with a considerably smaller active space (2 electrons in 6 orbitals) than ours. Yet, the agreement with our present SO-CASPT2 data is acceptable, the energy ordering of the excited states is the same in almost all cases, while the energy difference is mostly below 1000 cm$^{-1}$. The agreement is better with the SO-MRCI results from that study (obtained by the small 2 electrons in 4 orbitals active space, corrected for size-extensivity according to Davidson), though the latter results lack several high energy states.

Danilo et al. studied also the electronic states of hydrated NpO$_2^+$ modelled by the NpO$_2$(H$_2$O)$_5^+$ structure using SO-CASPT2 in conjunction with the smaller (2,4) active space. They showed that the H$_2$O ligand field around NpO$_2^+$ resulted generally in minor changes in the excitation energies, while the average deviation between the calculated and experimental excitation energies was 1234 cm$^{-1}$. The main advantage of this solvation model is, however, the intensity information. The ligands attached to NpO$_2^+$ can promote mixing of 5$f_\delta$ and 6$d_\delta$ orbitals, which can increase considerably certain transition probabilities. The computed oscillator strengths in Ref. 32 agree well with the experimental ones determined from the perchloric acid solution facilitating a reliable assignment.

As can be seen from Table IV, the Einstein coefficients of the NpO$_2^+$ molecule from our calculations are very different from the oscillator strength values of the NpO$_2$(H$_2$O)$_5^+$ model, confirming our above concern about the suitability of these intensity data of naked NpO$_2^+$ for the interpretation of condensed-phase spectra. On the other hand, the average deviation between the NpO$_2^+$ calculated and the experimental excitation energies is 1108 cm$^{-1}$, slightly better than for those of the NpO$_2$(H$_2$O)$_5^+$ model obtained by the smaller active space. Particularly, our low-energy data are in good agreement with experiment (cf. Table IV).

The latest (our present and those of Danilo et al.) computed data support generally the assignment proposed in the earlier HFSCC study by Infante et al. Our calculations support also the findings of Infante et al. that the 5$f_{\delta}$ orbital appears only in higher-lying excited states; hence, transitions lower in energy than 19 000 cm$^{-1}$ are unlikely to such orbitals.

Selected experimental and theoretical results of NpO$_2^{2+}$ are compared in Table V. In the experimental spectra, five bands (two in solution and five in the Cs$_2$UO$_2$Cl$_4$ crystal) have been identified as 5$f_\delta$-5$f_\delta$ electronic transitions from the ground state to low-lying excited states. The assignments of the charge transfer bands between 13 000 and 20 000 cm$^{-1}$ have been done in terms of symmetry on the basis of crystal and Zeeman effect and magnetic circular dichroism measurements on the Cs$_2$UO$_2$(NO$_3$)$_3$ crystal and semi-empirical calculations.

The theoretical studies compared in Table V include computations on the naked NpO$_2^{2+}$ ion and on the NpO$_2$Cl$_2$ complex. The whole spectrum range covered by the available experimental data has been investigated in three studies: in the early SO-CI one by Matsika and Pitzer, in the recent SO-RASPT2 study of Su et al., and in the present SO-CASPT2...
TABLE IV. Computed vertical excitation energies (cm$^{-1}$) of NpO$_2^+$ compared with the spectra in aqueous perchloric acid solutions.

| State | SO-CI | SO-MRCI | IHFSCC | SO-CASPT2 | SO-CASPT2 | Expt.e | Expt.f |
|-------|-------|---------|--------|-----------|-----------|-------|-------|
|        | E     | E       | E      | E         | E         | E     | Energies |
| 0$_g$  | 3.366 | 3.143   | 2.527  | 2.364     | 3.169     | 2.326 | 0       |
| 1$_g$  | 4.938 | 5.283   | 4.102  | 4.722     | 4.949     | 4.243 | 15.5    |
| 5$_g$  | 4.721 | 6.342   | 5.379  | 6.528     | 6.144     | 6.585 | 0       |
| 0$_g$  | 9.708 | 10.734  | 8.628  | 9.177     | 9.275     | 10.101| 0.4     |
| 1$_g$  | 9.076 | 10.469  | 8.929  | 9.687     | 9.755     | 9.719 | 15.60   |
| 0$_g$  | 9.537 | 11.829  | 9.378  | 10.068    | 10.382    | 11.094| 0.2     |
| 2$_g$  | 11.187| 12.392  | 10.056 | 10.697    | 10.992    | 11.740| 953.8   |
| 0$_g$  | 8.867 | 11.574  | 9.690  | 11.816    | 11.253    | 12.135| 0       |
| 0$_g$  | 14.415| 16.628  | 14.105 | 15.299    | 15.869    | 16.231| 0.1     |
| 0$_g$  | 15.249| 18.394  | 14.422 | 14.533    | 16.011    | 16.373| 0       |
| 0$_g$  | 16.156| 18.321  | 15.031 | 16.678    | 17.051    | 17.832| 65.1    |
| 0$_g$  | 19.647| 19.170  | 16.551 | 18.017    | 18.289    | 18.918| 0.5     |
| 0$_g$  | 24.834| 19.735  | 19.883 | 19.510    | 79.499    | 0     |
| 0$_g$  | 22.031| 22.530  | 19.761 | 21.496    | 22.521    | 21.930| 0       |
| 0$_g$  | 21.672| 22.045  | 18.992 | 21.041    | 20.911    | 22.408| 280     |
| 0$_g$  | 23.327| 22.649  | 20.035 | 23.813    | 22.923    | 25.728| 0       |
| 0$_g$  | 23.649| 23.187  | 21.852 | 22.879    | 22.923    | 0     |
| 0$_g$  | 26.592| 25.119  | 25.778 | 25.400    | 31.960    | 0     |
| 0$_g$  | 23.079| 25.436  | 25.826 | 27.046    | 27.916    | 0     |
| 0$_g$  | 27.494| 27.916  | 0     |
| 0$_g$  | 32.809| 30.846  | 116    |
| 0$_g$  | 32.809| 29.649  | 32.248 | 0         | 31.032   | 0.2   |

a SO-CI computations of Matsika and Pitzer.37
b From Ref. 32 using (2,4), (2,6), and (2,4) active spaces in the SO-MRCI and the two SO-CASPT2 calculations, respectively.
c IHFSCC computations of Infante et al.30
d Present computations including the Einstein coefficients (a.u.) for excitations from the ground state.
e 1M perchloric acid solution measured by Waggener17 interpretation revised by Eisenstein and Pryce.27 Additional experimental peaks: 16 100 cm$^{-1}$ (3Φ$_2$), 19 360 (Π$_1$), 21 700 (3Λ$_3$).
f 0.1 M perchloric acid solution measured by Matsika et al.19
Oscillator strength $\times 10^{-7}$ obtained with the (2,4) active space.
g Oscillator strength $\times 10^{-7}$.31
TABLE V. Computed excitation energies (cm⁻¹) of NpO₂⁺ and NpO₂Cl₂⁻ compared with experimental data.

|            | SO-CI IHFSCC | SO-RASPT2 | SO-CASPT2 | Experimental | SO-CI IHFSCC | SO-RASPT2 | SO-CASPT2 |
|------------|--------------|-----------|-----------|--------------|--------------|-----------|-----------|
| State      | E₁           | E₂        | E₃        | T₆          | E₁           | E₂        | E₃        | E₁           | E₂        | E₃         | E₁           | E₂        | E₃         |
| 2.5_u      | 0            | 0         | 0         | 0           | 0            | 0         | 0         | 0            | 0         | 0          | 0            | 0         | 0          |
| 1.5_u      | 447          | 3544      | 3221      | 3503        | 3011         | 2426      | 9         | 1000         | 1156      | 1055       | 944          | 1112      | 13264      |
| 3.5_u      | 6565         | 7227      | 7225      | 6107        | 8092         | 8158      | 49        | 6760         | 6459.0     | 6880       | 7738         | 5767      | 7759       |
| 2.5_u      | 5515         | 8929      | 8565      | 7798        | 9192         | 8241      | 537       | 8180         | 9420.2     | 7990       | 9137         | 6658      | 8600       |
| 3.5_u      | 12622        |           |           | 9498        | 9293        | 105        |           | 13918.1      | 13264.9    |           | 11127        |           |           |
| 0.5_u      | 15668        |           |           | 13816       | 12813       | 0         |           | 16072.5      | 15406.4    |           | 14375        |           |           |
| 4.5_u      | 15418        |           |           | 12490       | 12613       | 0         |           | 16092.6      | 15683      |           | 14122        |           |           |
| 1.5_u      | 16664        |           |           | 15015       | 14663       | 2         |           | 17967.7      | 16799.8    |           | 15330        |           |           |
| 1.5_u      | 25844        | 29441     |           | 19337       | 19759       | 53        |           | 17843.6      | 17241.4    | 20857       | 17129        |           |           |
| 1.5_u      | 21580        | 17282     | 21093     | 19510.2     | 19375.2     |           | 18774      |               |            |            |               |            |            |
| 1.5_u      | 28909        | 33856     | 34947     | 19318       | 24913       | 0         |           | 20816.3      | 20080.8    | 26305       | 20134        |           |           |

1 Vertical excitation energies from SO-CI computations of Matsika and Pitzer.²⁹
2 Vertical excitation energies from IHFSCC computations of Infante et al.³⁰
3 Vertical excitation energies from SO-CASPT2 calculations of Gendron et al.³¹ For NpO₂Cl₂⁻, they used an embedding potential obtained from DFT calculations.
4 Adiabatic excitation energies from SO-RASPT2 calculations using restriction schemes of S(2,4) and S(2,2) for NpO₂⁺ and NpO₂Cl₂⁻, respectively.³²
5 Vertical excitation energies from SO-CASPT2 calculations of Gendron et al.²⁹ using a (7,10) active space.
6 Vertical excitation energies from the present computations and the Einstein coefficients (a.u.) for excitations from the ground state.
7 From aqueous HCl solution.²⁰
8 Solid state spectrum, NpO₂⁺ doped into Cs₂UO₂(NO₃)₃ crystal.²³,²⁴
9 Solid state spectrum, NpO₂⁺ doped into Cs₂UO₂Cl₄ crystal.²³,²⁴
10 These energies were assigned to acceptor states with 0_5 character in Ref. 12.

Calculations by us. From these studies, Su et al. calculated both NpO₂⁺ and NpO₂Cl₂⁻, providing information on the effect of chloride ligands on the transition energies. Another advantage of this study (making it the best model for the doping experiment of NpO₂⁺ into Cs₂UO₂Cl₄ crystals³¹,³²) is the evaluation of the adiabatic transition energies. As can be expected, this study achieved the best average deviation (947 cm⁻¹) from experiment. Those of the SO-CI and SO-CASPT2 energies of the naked NpO₂⁺ are around 2400 cm⁻¹. Considering the 0-10 000 cm⁻¹ region of the spectrum, the best agreement with the experimental data of Cs₂UO₂Cl₄ (515 cm⁻¹) has been obtained by Gendron et al., who computed only the three lowest excitations of this molecule using SO-CASPT2.³³ We note that the better agreement in the latter limited study, the following character of CASPT2 may also contribute: the energies of excited states become less accurate with increasing number of states considered in the state-averaged calculations.

The assignments of the experimental transitions to the acceptor (excited) states are generally in agreement with our and in the listed literature studies.²⁴,²⁹-³¹,³³,³⁴ Instead of the Ω = 0.5₅ excited states suggested for the experimental transitions at 19 510 and 17 844 cm⁻¹ by Denning,²³,²⁴ our and the other recent computations predicted more suitable excited states with Ω values of 1.5.

B. NpO, NpO⁺, and NpO²⁺

The electronic ground states of these species were reported recently by Infante et al.¹² from SO-CASPT2 calculations. The ground and low-lying excited states are strongly mixed. We observed in the composition of the ground states of the three molecules determined in our present study some minor differences from those in Ref. 12 which, however, do not affect the Ω quantum number of these states. We attribute these differences to the inclusion of more states in the CASSCF and CASSI calculations, which result in more extensive mixing than occurred between the few ones (three states for each species) in Ref. 12.

The details of the electronic ground and excited states are given in the supplementary material.⁶,⁶ With exception of the ground states, nothing is known about these monoxides; therefore, we briefly discuss here a few important characteristics of their electronic structure.

The major components of the SO ground state of NpO arrive from the SO coupling of the ⁵Φ SF ground and ⁶Δ low-energy SF excited states (ca. 1000 cm⁻¹ above the SF ground state). Accordingly, the major Np orbital populations include the 7s and the four 5f (σ, π, δ, φ) orbitals. These are the major orbitals in the low-lying exciting states too, only with somewhat different contributions. The 6δ₎ orbitals appear with notable (but still minor) contribution above 13 000 cm⁻¹. Their importance is increased in the higher excited states. These characteristics can be compared with those of the isoelectronic PuO⁺.²⁷,²⁸ The latter species has a simpler electronic structure than NpO: it has one major (79%) contribution with no 7s occupation and also the 5f₅ orbitals have only a minor role in its electronic ground state. This character is preserved in the reported low-energy (0-3000 cm⁻¹) excited states of PuO⁺.⁷,⁷
the neutral NpO, became a minor contributor in the ion and gains importance in some high-energy excited states only. The same refers to the 6dδ orbitals too. Compared to the characteristics of isoelectronic UO, the main difference is the monoconfigurational character and dominant 7s contribution in the uranium oxide, in the ground state of which the 5fσ orbital plays no role.\textsuperscript{12,75} However, the 7s and 5fσ orbitals appear as minor contributions in some high-energy excited states of UO.\textsuperscript{73} The case is similar in the isoelectronic PuO\textsuperscript{2+} with a major (70\%) SF state of 5fσ\textsuperscript{2}, 5fσ\textsuperscript{1}, 5fσ\textsuperscript{1} character. In the ground and excited states of the latter species, 5fσ has been found as a minor contributor.\textsuperscript{12,74}

The SO ground state of NpO\textsuperscript{2+} consists mainly of the ^4I\textsubscript{SF} ground state with major Np 5fσ\textsuperscript{1}, 5fσ\textsuperscript{1}, 5fσ\textsuperscript{1} populations. The 5fσ

FIG. 2. Simulated gas-phase absorption electronic spectra of NpO, NpO\textsuperscript{+}, and NpO\textsuperscript{2+}.
orbital gains importance in the first excited state having a $^4\text{H}$ character, then in a few strongly mixed states above 8000 cm$^{-1}$. The 6$d_2$ orbital appears as minor contributor in strongly mixed excited states above 10 000 cm$^{-1}$. The only isoelectronic actinide oxide with available literature data is UO$^+$ with analogous ground and first excited states. However, the 5$f_0$ orbital seems to have a larger role in the excited states of UO$^+$ than found in NpO$^{2+}$.

The calculated electronic spectra for 298 K and for 3000 K are presented in Figure 2. In Tables VI–VIII, the most intense transitions for NpO, NpO$^+$, and NpO$^{2+}$, respectively, are compiled and characterized.

A brief comparison of the monoxide spectra and data with those of the dioxides reveals considerably more excited states and electronic transitions within the covered energy window of 0-35 000 cm$^{-1}$. The reason is the larger number of unbound Np valence electrons in the monoxides resulting in an increased number of possible electron configurations. Another characteristic of the monoxides is, as compared to the above discussed dioxides, the considerably more extensive mixing in the electronic states. The majority of the excited states consist of several electron configurations with a low contribution being impossible to pick a single electron configuration as dominant contribution. Thus, instead of excitations of well-
defined electrons to another orbital, the transitions in these species are characterized by transfer of small electron density fractions.

From the three species, the electronic spectra of NpO (Figure 2) are the most crowded, even at room temperature. There are four and five (at 298 K and 3000 K, respectively) very intense transitions between 25 000 and 33 000 cm$^{-1}$. All the listed significant transitions at 298 K occur from the ground state. The most intense excitation (at 26 694 cm$^{-1}$) corresponds to a population transfer from the 7s, 5f$_b$, and 5f$_a$ orbitals to 6d$_b$ and 5f$_c^*$, the latter meaning the 5f$_c$ orbital with opposite-sign magnetic quantum number with respect to the donor 5f$_a$.

At 3000 K, transitions from low-lying excited states (up to the fourth excited state at 2354 cm$^{-1}$) appear with considerable intensity. The most intense band in the covered range is the one computed at 30 398 cm$^{-1}$ representing a major 5f$_a$, 5f$_b$, 7s $\rightarrow$ 5f$_a^*$, 5f$_b^*$ charge transfer. The majority of the transitions involve the Np 7s orbital as donor and the 6d$_b$ orbital as acceptor. From the 5f orbitals, 5f$_b$ is the

| TABLE VII. Significant computed electronic transitions (cm$^{-1}$) of NpO$^{+}$ |   |
|----------------------------------|---|
| Energy | 298 K | 3000 K | Einstein | From$^b$ | To$^b$ | Main orbitals involved |
| 14 905 | 15 | 349 513 | 4(3) | 78(3) | 5f$_a$ $\rightarrow$ 7s |
| 17 363 | 24 | 402 772 | 3(2) | 102(2) | 5f$_a$, 5f$_b$ $\rightarrow$ 7s, 6d$_b$ |
| 17 950 | 5 | 538 741 | 2(1) | 109(1) | 5f$_a$, 5f$_b$, 5f$_c$ $\rightarrow$ 6d$_b$, 5f$_a$ |
| 18 063 | 25 | 418 070 | 3(2) | 111(2) | 5f$_a$, 5f$_b$ $\rightarrow$ 6d$_b$ |
| 19 744 | 22 | 492 002 | 4(3) | 147(3) | 5f$_a$, 5f$_b$, 5f$_c$ $\rightarrow$ 6d$_b$, 7s |
| 19 797 | 15 | 1 402 516 | 2(1) | 134(1) | 5f$_a$, 5f$_b$, 5f$_c$ $\rightarrow$ 6d$_b$, 7s |
| 19 916 | 4 | 25 | 364 050 | 2(1) | 136(1) | 5f$_a$, 5f$_b$, 5f$_c$, 5f$_d$ $\rightarrow$ 7s, 6d$_b$ |
| 20 373 | 100 | 91 | 1 053 352 | 1(0) | 136(1) | 5f$_a$, 5f$_b$, 5f$_c$, 5f$_d$ $\rightarrow$ 7s, 6d$_b$ |
| 21 822 | 6 | 43 | 626 053 | 2(1) | 162(2) | 5f$_a$, 5f$_b$, 5f$_c$, 5f$_d$ $\rightarrow$ 7s, 6d$_b$ |
| 22 225 | 67 | 61 | 709 038 | 1(0) | 161(1) | 5f$_a$, 5f$_b$, 5f$_c$, 5f$_d$ $\rightarrow$ 7s, 6d$_b$ |
| 22 334 | 9 | 59 | 848 473 | 2(1) | 170(2) | 5f$_a$, 5f$_b$, 5f$_c$, 5f$_d$ $\rightarrow$ 7s, 6d$_b$ |
| 24 764 | 27 | 450 982 | 3(2) | 244(2) | 5f$_a$, 5f$_b$ $\rightarrow$ 6d$_b$, 7s |
| 27 322 | 47 | 22 | 499 279 | 1(0) | 283(1) | 5f$_a$, 5f$_b$ $\rightarrow$ 6d$_b$, 7s |
| 28 499 | 23 | 10 | 238 825 | 1(0) | 306(1) | 5f$_a$, 5f$_b$ $\rightarrow$ 7s, 5f$_a$, 6d$_b$ |
| 28 738 | 100 | 3 106 203 | 5(4) | 376(3) | 5f$_a$, 5f$_b$ $\rightarrow$ 6d$_b$ |
| 28 744 | 52 | 1 623 235 | 5(4) | 377(4) | 5f$_a$, 5f$_b$, 5f$_c$ $\rightarrow$ 6d$_b$ |
| 29 877 | 23 | 708 032 | 5(4) | 410(3) | 5f$_a$, 5f$_b$ $\rightarrow$ 6d$_b$ |
| 33 447 | 24 | 395 158 | 3(2) | 447(2) | 5f$_a$, 5f$_b$ $\rightarrow$ 6d$_b$, 7s |
| 33 519 | 44 | 746 053 | 3(2) | 448(1) | 5f$_a$, 5f$_b$ $\rightarrow$ 6d$_b$, 5f$_a$ |
| 34 061 | 82 | 1 846 990 | 4(3) | 463(2) | 5f$_a$, 5f$_b$, 6d$_b$, 5f$_c$, 6d$_a$ |
| 34 680 | 21 | 707 611 | 3(2) | 463(2) | 5f$_a$, 5f$_b$, 6d$_b$, 5f$_a$ |
| 34 786 | 11 | 10 | 114 917 | 1(0) | 452(1) | 5f$_a$, 5f$_b$ $\rightarrow$ 7s, 5f$_a$ |

$^a$The energies of transitions are given in cm$^{-1}$, the relative intensities in % (using a threshold of 1%), and the Einstein coefficients in a.u.

$^b$The spin-orbit states defining the transitions; $\Omega$ values in parentheses; for other details of the states, see the supplementary material STables 10 and 11.$^{76}$

TABLE VIII. Selected significant computed electronic transitions (cm$^{-1}$) of NpO$^{2+}$ |   |
|----------------------------------|---|
| Energy | 298 K | 3000 K | Einstein | From$^b$ | To$^b$ | Main orbitals involved |
| 8 719 | 1 | 1 | 6 184 | 1(4.5) | 9(3.5) | 5f$_a$ $\rightarrow$ 5f$_b$ |
| 9 153 | 2 | 68 537 | 4(1.5) | 23(1.5) | 5f$_a$, 5f$_b$ $\rightarrow$ 5f$_a$, 5f$_b$ |
| 11 193 | 2 | 185 586 | 6(0.5) | 37(0.5) | 5f$_a$ $\rightarrow$ 5f$_b$ |
| 11 211 | 2 | 9 853 | 1(4.5) | 16(3.5) | 5f$_a$, 5f$_b$ $\rightarrow$ 5f$_a$, 5f$_b$, 6d$_b$ |
| 19 733 | 4 | 20 844 | 1(4.5) | 46(5.5) | 5f$_a$, 5f$_b$ |
| 22 285 | 2 | 37 469 | 2(3.5) | 65(2.5) | 5f$_a$, 5f$_b$, 6d$_b$ $\rightarrow$ 5f$_a$, 5f$_b$ |
| 23 904 | 2 | 9 500 | 1(4.5) | 61(5.5) | 5f$_a$ $\rightarrow$ 5f$_b$ |
| 27 205 | 10 | 514 373 | 5(5.5) | 112(6.5) | 5f$_a$ $\rightarrow$ 6d$_b$ |
| 27 273 | 100 | 510 090 | 1(4.5) | 80(5.5) | 5f$_a$ $\rightarrow$ 6d$_b$ |
| 27 672 | 4 | 77 239 | 2(3.5) | 104(2.5) | 5f$_a$, 6d$_b$ $\rightarrow$ 5f$_a$ |
| 28 553 | 2 | 36 792 | 2(3.5) | 109(3.5) | 5f$_a$, 6d$_b$ $\rightarrow$ 5f$_a$ |

$^a$The energies of transitions are given in cm$^{-1}$, the relative intensities in % (using a threshold of 1%), and the Einstein coefficients in a.u.

$^b$The spin-orbit states defining the transitions; $\Omega$ values in parentheses; for other details of the states, see the supplementary material STables 12 and 13.$^{76}$
most frequently involved in these processes. In the very high-energy transitions (above 28 700 cm\(^{-1}\)), the donor role of 7s is decreased, and it appears instead as acceptor in a few excitations.

The electronic spectra of NpO\(^+\) are considerably less crowded than those of NpO, but still include plenty of weak transition lines. Similarly to NpO, the most intense transitions appear at and above 20 000 cm\(^{-1}\). Most excitations in the 298-K spectrum occur from the ground electronic state, but because of the notable population of the close-lying first excited state (at 457 cm\(^{-1}\), cf. Table VII), transitions from this state appear with some intensity (up to 15\%) too. The most intense line (at 20 733 cm\(^{-1}\)) corresponds to a 5f\(_6\), 5f\(_6\) \(\rightarrow\) 5f\(_7\), 7s \(\rightarrow\) 6d\(_0\) population transfer from the ground electronic state. Though this transition is very intense in the spectrum at 3000 K too, the main one there (at 28 738 cm\(^{-1}\)) occurs from the fourth excited state with somewhat different population transfer characteristics (5f\(_6\), 5f\(_6\) \(\rightarrow\) 6d\(_0\)). Regarding the role of Np atomic orbitals in the transitions, the main difference compared to neutral NpO is the lack of 7s orbital from the donor (ground and low-lying excited) states. Instead, 7s appears as an important acceptor in ca. half of the acceptor states. The most frequent donor orbitals are 5f\(_6\) and 5f\(_8\), while the most frequent acceptor orbital is 6d\(_0\), accompanied in several cases by 7s and 5f\(_6\).

In contrast to the previous two monoxide species, the computed electronic spectra of the NpO\(^2+\) ion at both 298 K and 3000 K are poor of intense transitions. They include a single intense line only (at 27 273 cm\(^{-1}\), cf. Figure 2 and Table VIII) attributed to a 5f\(_9\) \(\rightarrow\) 6d\(_0\) population transfer. The Einstein coefficient of this transition is comparable to the intense ones in the spectra of NpO but is smaller by ca. one order of magnitude than those of NpO\(^+\). Differences with respect to NpO and NpO\(^+\) appear in the Np orbitals important in the transitions: In NpO\(^2+\), the 5f\(_9\) orbital does not play an important role; the most frequent donor orbital is 5f\(_4\). The acceptor ones cover 6d\(_n\), 6d\(_n\) and all the four types of 5f. As 7s is poorly populated in NpO\(^2+\), it does not have any important role in its transitions.

IV. CONCLUSIONS

We studied the low-lying excited states and corresponding gas-phase electronic spectra of the neutral and ionic NpO and NpO\(_2\) molecules. Our computations at the SO-CASPT2 level of theory elucidated the parameters and characters of electronic transitions. Spectral intensities were estimated on the basis of the computed Einstein coefficients for room temperature (298 K) and for 3000 K, being more relevant for the gas-phase experiments. From the six studied species, the dioxides (NpO\(_2\), NpO\(^+\), NpO\(^{2+}\)) and NpO\(^{2+}\) have quite simple electronic spectra possessing only a few intense peaks. On the other hand, the spectra of NpO and NpO\(^+\) are very dense. The electronic states of these two species are strongly mixed and in several cases only small population transfers between various Np orbitals could be recognized. The computed vertical transition energies show good agreement with the previous results on NpO\(^{2+}\) and NpO\(^{2+}\).

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