Theoretical Prediction of Rhenium Separation from Ammonium Perrhenate by Phonon–Photon Resonance Absorption

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ABSTRACT: Rhenium (Re) is an extremely rare and precious element that is mainly used in the construction of aerospace components and satellite stations. However, an efficient and simple method for preparing Re has yet to be devised. To this end, we investigated the vibrational spectrum of ammonium perrhenate (NH₄ReO₄) using the CASTEP code based on first-principles density functional theory. We assigned the infrared (IR) absorption and Raman scattering spectra for NH₄ReO₄ using a dynamic process analysis of optical branch normal modes. We examined the IR-active peaks of Re-related vibrational modes in detail and found that the typical IR peak at approximately 914 cm⁻¹ is due to the Re–O bond stretching. Thus, we posit that strong terahertz laser irradiation of NH₄ReO₄ at 914 cm⁻¹ will lead to sufficient resonance absorption to cleave its Re–O bonds. This method could potentially be used to efficiently separate Re from its oxides.

INTRODUCTION

Rhenium (Re) is an extremely rare and precious element with high melting and boiling points. It is also the only refractory metallic element that does not react with carbon.1–4 Consequently, Re has important applications in petroleum and aerospace industries. It is mostly used in the form of superalloys (78%), with the remainder used in catalysts (14%) and other applications (8%).5 Thus, Re superalloys are critical constituents of aerospace components and satellite stations. For example, the Re–nickel superalloy is the core material of modern jet engines, turbine disks, and other important structural components.6–9 Moreover, the core components of the engine of China’s first Mars probe, “Tianwen-1,” are made of the Re superalloy. The world’s demand for Re has therefore increased dramatically in recent years, and the mining and recovery of Re resources are of great strategic importance to many countries worldwide.

At present, the separation of Re from other metals and oxides in aqueous solution is an important step in the production of Re from ores and secondary raw materials and is performed by solvent extraction10–16 or ion exchange.17–19 This is followed by a high-temperature reduction and a complex deoxidation process, for which high-temperature-resistant equipment is required. An efficient and simpler method for the isolation of Re has yet to be developed.20 There has also been a lack of research on the recovery of Re from secondary resources such as waste catalysts and waste alloys. Thus, there is a need for the development of such recovery technologies that are suitable for large-scale and industrial applications, and continued research in this area is crucial for ensuring future demand for Re can be met.21

Many spectroscopic studies have focused on ammonium perrhenate (NH₄ReO₄),22–31 which is the most common commercial form of Re. Korppi-Tommola et al., for example, examined the temperature dependence of the Raman spectrum of NH₄ReO₄.23 In a related work, Gassman et al. fabricated sodium borosilicate sunglasses containing Re and used confocal Raman microscopy to study their vibrational spectra. This showed that the spectra of ReO₄⁻ exhibited different Raman bands to those of persulfate.28 Borowiec et al. obtained the Raman spectrum of NH₄ReO₄ which they sulfated at room temperature to form Re disulfide.29 Brown et al. studied the lattice structure of NH₄ReO₄ — specifically, the thermal contraction of the a-lattice parameter and the substantial thermal expansion of the c-lattice parameter — and the enhanced nuclear quadrupole relaxation and increased specific heat capacity of NH₄ReO₄.30,31

However, despite the above experimental and computational studies of NH₄ReO₄ there is a dearth of theoretical methods for the assignment of peaks in NH₄ReO₄ spectra. Thus, in this study, we simulated the vibrational spectra of NH₄ReO₄ and used normal mode analysis to identify the Re-related peaks.

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Our identification of the Re-related vibrational peaks allowed us to determine the IR-active modes of Re in previously reported experimentally obtained spectra of NH₄ReO₄. Based on these findings, we propose a novel method for the separation of Re from its oxides that exploits photon–phonon resonance absorption.

METHODS

We used the CASTEP code for geometric optimization and phonon calculations, based on first-principles density functional theory. Due to the large change in the gradient of electron density in NH₄ReO₄, we employed the generalized gradient approximation of the Perdew–Burke–Ernzerhof exchange–correlation functional. The convergence tolerance value of the energy and self-consistent field was set to $1 \times 10^{-9}$ eV/atom. The energy cutoff was set to 830 eV and a $3 \times 3 \times 3$ $k$-point mesh was used. The norm-conserving pseudo-potential was applied to calculate the phonons via the linear response method, and IR and Raman intensity calculations were also performed. Thus, we obtained simulated IR and Raman spectra that were suitable for comparison with spectral data previously reported by others, thereby enabling us to assign Re-related peaks in these spectra via a dynamic process analysis of each normal-mode vibration.

RESULTS AND DISCUSSION

NH₄ReO₄ crystallizes with the Scheelite (CaWO₄) structure. Its space group is $I4_1/a$, with two formula units per primitive cell. According to the group theory, both ReO₄⁻ and NH₄⁺ occupy $S_i$ sites, with N and Re in Wyckoff positions $a$ and $b$, respectively, and O and H atoms occupying general Wyckoff $f$ positions. A factor group analysis of NH₄ReO₄ was made using Adams’ tables. The 60 vibrational normal modes of NH₄ReO₄ are classified as $4A_u + 6B_u + 4E_u + 6A_g + 4B_g + 4E_g$ internal modes, $2A_u + 2B_u + 4E_u + A_g + 2B_g + 3E_g$ external modes, and $A_u + E_u$ acoustic modes. As both ReO₄⁻ and NH₄⁺ occupy $S_i$ sites in the lattice, their modal analyses are the same: each pair of identical ions gives rise to $2A_u + 3B_u + 2E_u + 3A_g + 2B_g + 2E_g$ internal modes in the primitive cell. These can be correlated to the “free” ion vibrations $v_1$ ($A_1$), $v_2$ ($E$), $v_3$, and $v_4$ ($F_2$). According to one of the Raman spectra of ammonium perrhenate NH₄ReO₄, the $A_1$ mode of the “free” ion should remain a singlet, while the $E$ and $F_2$ modes should be split into doublets.

The external optical modes are classified as rotatory (or librational) ($v_5$) lattice modes or translational ($v_6$) lattice modes. Given the substantial difference between the ionic masses of NH₄⁺ and ReO₄⁻, it is reasonable to separate the external modes into two groups describing the motions of the two ions. The rotational and translational motions of a “free” ion of symmetry $T_d$ represent those of species $F_i$, and $F_2$.

Figure 1 shows simulated IR, Raman, and phonon density of states (PDOS) spectra of NH₄ReO₄. Based on the harmonic approximation, there are 57 optical branch lattice waves ($20 \times 3 - 3$) for a 20-molecular primitive cell. That is, there are fewer than 57 normal-mode phonon–phonon couplings with IR light. Due to the special symmetry of NH₄ReO₄, its IR- and Raman-active modes are complementary, as shown in Table 1.

Korppi-Tommola et al. reported the Raman spectrum of NH₄ReO₄ in 1978 and assigned the peaks by comparing the vibrational peaks of NH₄ReO₄ and ND₄ReO₄. They concluded that the peaks at 49, 67, 120, and 135 cm⁻¹, which are not affected by deuteration, are mainly caused by the vibrations of ReO₄⁻. In addition, they found that the peaks at 49 and 67 cm⁻¹ are ion-cluster $v_2$ modes, whereas the peaks at 120 and 135 cm⁻¹ are $v_1$ modes. Park et al. measured the Raman spectrum of $^{15}$NH₄ReO₄ within which they identified two sets of ReO₄⁻ vibrational peaks (50/69 and 122/144 cm⁻¹). Our simulations identified six Raman-active modes at similar frequencies to those above: 47(2), 54, 107(2), and 120 cm⁻¹. We performed dynamic process analysis that revealed that three of these modes [47(2) and 54 cm⁻¹] represent translational motions of ions between different NH₄⁺ and ReO₄⁻ ion clusters. We also identified two IR-active degenerate modes at 79 cm⁻¹ and a Raman- and IR-inactive mode at 128 cm⁻¹. The six modes 79(2), 107(2), 120, and 128 cm⁻¹ are primarily librational modes of ReO₄⁻ clusters. Two typical modes (47 and 120 cm⁻¹) are shown in Figure 2.

Thompson et al. studied the vibrational spectra of NH₄ReO₄ and the double complex salt Pd(NH₃)₄(ReO₄)₂. They proposed that the vibrational modes in the low-frequency region from 100 to 600 cm⁻¹ are attributable to skeletal vibration modes, whereas those in the higher frequency region (600–1200 cm⁻¹) are primarily ReO₄⁻ vibrations. Tommola et al. assigned the peaks of NH₄ReO₄ at 189 and 210 cm⁻¹ to $v_1$. Park et al. identified the Raman spectral peaks of NH₄ReO₄ at 191 and 214 cm⁻¹. According to our work, the normal modes at 170(2) and 177 cm⁻¹ are IR-active, whereas the normal modes at 176(2) and 189 cm⁻¹ are Raman-active and that all of these normal modes are translational modes of NH₄⁺.

Thompson et al. reported an NH₄ReO₄ IR spectral peak at approximately 290 cm⁻¹, which they attributed to the O–Re–O bending. Korppi-Tommola et al. assigned an NH₄ReO₄ Raman spectral peak at 264 cm⁻¹ to $v_2$. Park et al. found two Raman spectral peaks (at 265 and 276 cm⁻¹). According to Table 1, 10 modes from 292 to 345 cm⁻¹ correspond to ReO₄⁻ librational modes. In contrast, six modes (at 403(2), 404, 405(2), and 413 cm⁻¹) are librations of NH₄⁺. See one example at 404 cm⁻¹ in Figure 3.

Korppi-Tommola et al. suggested that the Raman spectral peaks at 893 and 910 cm⁻¹ are associated with a ReO₄⁻ $v_3$ ($F_2$) vibration mode. Similarly, Thompson attributed the strong IR spectral peak at 914 cm⁻¹ to antisymmetric Re–O stretching. Gonzalez-Rodriguez deduced that the IR spectral peak at 913 cm⁻¹ was related to ReO₄⁻ by comparing the IR spectra of NH₄ReO₄ and potassium perrhenate (KReO₄). Moreover, this peak is very close to the peak at 910 cm⁻¹ for ReO₄⁻ in the IR spectrum of the [(CuCl)₂PF₆](ReO₄)·3H₂O complex, which was obtained by Cao. In the current
Table 1. Comparison of Calculated Raman- or IR-Active Normal Modes for NH₄ReO₄ (the Number in Brackets in the First Column Indicates the Degeneracy) with Reported Raman and Infrared (IR) Spectroscopy Data (cm⁻¹)

| normal modes | Raman | IR |
|--------------|-------|----|
| 47(2) Raman  | ref 23 | 49 | skeletal translation |
| 54 Raman     | ref 37 | 67 | skeletal translation |
| 79(2) IR     | ref 38 | 69 | skeletal translation |
| 107(2) Raman | ref 38 | 120 | ReO₄⁻ libration |
| 120 Raman    | ref 39 | 135 | ReO₄⁻ libration |
| 128          |       | ReO₄⁻ libration |
| 170(2) IR    |       | NH₄⁺ translation |
| 176(2) Raman |       | NH₄⁺ translation |
| 177 IR       |       | NH₄⁺ translation |
| 189 Raman    |       | 210 | NH₄⁺ translation |
| 292 IR       |       | 290 | ReO₄⁻ bending |
| 301(2) IR    |       | 263 | ReO₄⁻ bending |
| 318 Raman    |       | 265 | ReO₄⁻ bending |
| 320 Raman    |       | 276 | ReO₄⁻ bending |
| 329(2) Raman |       | 335 | ReO₄⁻ bending |
| 337 Raman    |       | 351 | ReO₄⁻ bending |
| 339          |       | 351 | ReO₄⁻ bending |
| 345 IR       |       | 914 | NH⁺ libration |
| 403(2) IR    |       | 913 | NH⁺ libration |
| 404 Raman    |       | 969 | NH⁺ libration |
| 405(2) Raman |       | 1450 | NH⁺ libration |
| 413          |       | 1448 | ReO₄⁻ stretching |
| 942(2) Raman | 893   | 914 | ReO₄⁻ stretching |
| 947 IR       | 913   | 913 | ReO₄⁻ stretching |
| 950(2) IR    | 913   | 913 | ReO₄⁻ stretching |
| 952 Raman    | 910   | 913 | ReO₄⁻ stretching |
| 1014 Raman   | 969   | 914 | ReO₄⁻ stretching |
| 1015         |       | 1450 | NH⁺ bending |
| 1432(2) IR  | 1450  | 1448 | NH⁺ bending |
| 1450 IR      | 1450  | 1448 | NH⁺ bending |
| 1451(2) Raman| 1431  | 1440 | NH⁺ bending |
| 1468 Raman   | 1438  | 1440 | NH⁺ bending |
| 1684 Raman   | 1658  | 1658 | NH⁺ bending |
| 1687 Raman   | 1658  | 1658 | NH⁺ bending |
| 1692 IR      | 1704  | 1704 | NH⁺ bending |
| 1704         | 1704  | 1704 | NH⁺ bending |
| 1704         | 1704  | 1704 | NH⁺ bending |
| 1704         | 1704  | 1704 | NH⁺ bending |
| 3084         | 3125  | 3150 | NH⁺ stretching |
| 3085 Raman   | 3128  | 3130 | NH⁺ stretching |
| 3112(2) Raman| 3128  | 3130 | NH⁺ stretching |
| 3113(2) IR  | 3128  | 3130 | NH⁺ stretching |
| 3123 Raman   | 3128  | 3130 | NH⁺ stretching |
| 3124 IR      | 3225  | 3150 | NH⁺ stretching |
| 3124 IR      | 3225  | 3150 | NH⁺ stretching |

That means, the phonon–photon resonance absorption at this peak is highly efficient. Provided a terahertz laser at this frequency be supplied to NH₄ReO₄, the direct energy absorption of the Re–O bond will result in energy level transitions and facilitate the Rhenium separation from NH₄ReO₄.

In the higher energy region from 1432 to 3124 cm⁻¹, we found that all of the vibrational modes are related to NH₄⁺ clusters, due to the lower mass of this ion. Gonzalez-Rodriguez et al. also compared the IR spectra of NH₄ReO₄ and KReO₄. This revealed that the peaks present in both spectra correspond to ReO₄⁻ and that the peaks of NH₄ReO₄ at frequencies from 1448 to 3004 cm⁻¹ are those for NH₄⁺. Similarly, Devarajan et al. observed two Raman peaks—at 1438 and 3182 cm⁻¹—for NH₄ReO₄, which they assigned to v₁ (F₂) stretching and v₂ (F₂) bending modes, respectively, of NH₄⁺. Thompson et al. and Gonzalez-Rodriguez et al. observed an IR spectrum peak for NH₄ReO₄ at approximately 1450 and 1448 cm⁻¹, respectively. Korppi-Tommola et al. observed Raman spectrum peaks for NH₄ReO₄ at 1431, 1438, and 1658 cm⁻¹, and Park et al. observed Raman spectrum peaks for NH₄ReO₄ at 1433, 1440, and 1658 cm⁻¹. In our simulations, 10 modes in the region from 1432 to 1704 cm⁻¹ represent bending vibrations of NH₄⁺ ions.

At frequencies above 3000 cm⁻¹, several distinct vibrational peaks can be seen in both the IR and Raman spectra of NH₄ReO₄, which correspond to the stretching vibrations of the N–H bond of NH₄⁺. Korppi-Tommola et al. found a Raman spectrum peak at 3128 cm⁻¹, while Park et al. found a Raman spectrum peak at 3128 cm⁻¹, which they assigned to v₁ (F₂) stretching and v₂ (F₂) bending modes, respectively, of NH₄⁺.}

study of NH₄ReO₄ we identified these NH₄ReO₄ peaks at similar frequencies to those above: four Raman-active modes [942(2), 952, and 1014 cm⁻¹], three IR-active modes [947 and 950(2) cm⁻¹], and one IR- and Raman-inactive mode at 1015 cm⁻¹ (Table 1). Our dynamic analysis confirmed that these eight modes are all related to Re=O stretching.

The IR-active mode at 947 cm⁻¹ corresponds to the experimental IR peak at around 914 cm⁻¹. The dynamic process of Re=O antisymmetric stretching at 947 cm⁻¹ can be seen from the Supporting Information file. Interestingly, while this mode shows the second intensity in the simulated spectrum, the experiments from refs 38 and 39 presented that this peak shows the highest intensity in the IR spectrum.
spectrum peak at 3130 cm\(^{-1}\), which they assigned to \(v_1\) (\(A_1\)) and also found a Raman peak at 3182 cm\(^{-1}\), which they assigned to \(v_1\) (\(E\)). Thompson et al.\textsuperscript{38} observed a significant IR spectrum peak at 3225 cm\(^{-1}\) and Gonzalez-Rodriguez et al.\textsuperscript{39} observed an IR peak at 3150 cm\(^{-1}\). In our work, these eight modes represent various N–H stretching modes. For example, see the vibrational mode at 3124 cm\(^{-1}\), as shown in Figure 3.

\section{CONCLUSIONS}

We calculated the normal modes of NH\(_4\)ReO\(_4\) and performed a dynamic process analysis of the calculated modes, which revealed that the compound forms two ion clusters that vibrate almost independently. In the lowest frequency region, three modes from 47 to 54 cm\(^{-1}\) are skeletal deformations, in which all of the ion clusters exhibit translational motions. Next, those from 79 to 128 cm\(^{-1}\) are mainly ReO\(_4\)\(^{-}\) librations, whereas those from 170 to 189 cm\(^{-1}\) are vibrational modes related to translational motions of NH\(_4\)\(^+\). The next bands of modes, from 292 to 345 cm\(^{-1}\), are various bending modes of ReO\(_4\)\(^{-}\), whereas those from 403 to 413 cm\(^{-1}\) are vibrational modes representing all of the possible NH\(_4\)\(^+\) rotations. In the two high-energy bands from 1432 to 3124 cm\(^{-1}\), all of the modes represent NH\(_4\)\(^+\) bending and stretching vibrations. Each vibrational mode is unique, and the degenerate modes have different vibrational directions.

We confirmed that the modes from 942 to 1015 cm\(^{-1}\) represent O–Re stretching; the significant IR spectrum peaks at approximately 914 cm\(^{-1}\) represent one kind of O–Re stretching. The Supporting Information Video shows the dynamic process of the O–Re stretching. The IR-active vibrational mode is high-intensity, which means that this mode resonantly absorbs a large amount of IR radiation.

Re is present in molybdenum and copper ores and is produced commercially as a byproduct of the metallurgical processing of these ores. Specifically, the Re in the ores is the Re\(_2\)O\(_7\) powder, which is subsequently dissolved in aqueous solution to form ReO\(_4\)\(^{-}\). As mentioned, two chemical methods are used for the extraction of Re as solvent extraction\textsuperscript{10–16} and ion exchange,\textsuperscript{17–19} and these are currently used in industrial processes.\textsuperscript{41,42} Our findings suggest that a strong terahertz laser irradiation of ReO\(_4\)\(^{-}\) at 914 cm\(^{-1}\) may result in resonance absorption sufficient to cleave its Re–O bonds, thereby facilitating the separation of Re.

\section{ASSOCIATED CONTENT}

\subsection{Supporting Information}

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06744.

Vibration mode of NH\(_4\)ReO\(_4\) at 914 cm\(^{-1}\) (MP4)

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\subsection{Notes}

The authors declare no competing financial interest.

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