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Identification and Structures of Matrix-Isolated Ruthenium Oxide Molecules from Infrared Spectra

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Matrix isolation and FTIR spectroscopy were used to study isotopically substituted ruthenium oxide molecules in argon matrices at 14 K. The species studied were produced by sputtering argon gas mixed with $^{16}O_2$ and $^{18}O_2$ in various proportions flowing through a hollow cathode discharge using pure ruthenium as the hollow cathode. By varying the ^{16}O:^{18}O ratio as well as the O_2:Ar ratio, the various isotopomers of each ruthenium oxide product could be assigned to the observed vibrational bands in the IR absorption spectra. The characteristic pattern resulting from the seven naturally occurring isotopes of Ru was particularly helpful in the identification of overlapping spectra. Metal oxides observed were RuO, RuO_2, RuO_3, and RuO_4. Using isotopomer vibrational frequencies, the fundamental vibrational frequency and anharmonicity were determined for RuO and RuO_2. In addition, the geometry of RuO_2 and RuO_3 was determined. RuO_2 is bent with a bond angle of 149 ± 2°. RuO_3, within experimental error, appears to be trigonal planar. These are the first spectroscopic measurements reported for isolated RuO_2 and RuO_3 species. © 1989 Academic Press, Inc.

I. INTRODUCTION

In the course of an investigation of the photochemical decomposition of gaseous RuO_4 (*1*), it became evident that, depending on the varying conditions of photolysis, all of the simple lower oxides, RuO, RuO_2, and RuO_3, appear as transient gaseous species; the stable end products are the well known solid RuO_2 (*2, 3*) and the hitherto unknown solid RuO_3. The three above mentioned gaseous species have been identified previously and studied by mass spectrometric detection of the species generated in high-temperature gas effusion cells initially containing solid Ru or RuO_2 and low-pressure O_2 gas (*4*) and by other high temperature gas transport experiments (see (*4*)). Electronic emission band systems in the visible region have been observed for

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RuO formed in a Ru hollow cathode discharge in the presence of O_2 gas or in a DC arc (*5, 6*). The same bands have been observed by some of the present authors in gas phase absorption spectra (*1*). Neither RuO_2 nor RuO_3 have been previously observed spectroscopically either in the gas phase or in matrix isolation.

It was clearly desirable to better characterize the isolated molecules spectroscopically and toward this end we have investigated the infrared spectra in the bond stretching region for all of the simple Ru oxides (including RuO_4) in low-temperature Ar matrices using the sputtering techniques developed by one of the authors (D. W. Green) in his laboratory and using FTIR spectroscopy (*7, 8, 9*). We have also studied the low-temperature matrix infrared spectrum of RuO_4 deposited directly, without sputtering, from a RuO_4–Ar gas mixture; this latter spectrum is discussed separately in another communication (*10*).

In the sputtering experiments, matrices containing various mixtures of oxides are obtained. The different oxides were identified by fitting observed oxide isotopomer frequencies with frequencies calculated from normal coordinate analyses, as has been described in Ref. (*8*) for tungsten oxides.

II. EXPERIMENTAL PROCEDURE

The apparatus and experimental procedures are described in detail in Ref. (*7, 8, 9*) and in other papers listed therein. We give only additional information specific to the present ruthenium work.

Two hollow cathodes for the sputtering device were machined (using electric discharge machining) from a $\frac{1}{4}$-in. diameter rod of pure Ru produced by compressing and sintering the powdered metal at high temperatures and obtained from Englehart Industries. Mixtures of $^{18}O_2$ and $^{16}O_2$ and Ar were used in the sputtering process to produce mixtures of isotopomers of Ru oxides, natural Ru being a mixture of seven stable isotopes. The mass numbers (and isotopic abundances in percent) are 96 (5.5); 98 (1.9); 99 (12.7); 100 (12.6); 101 (17.1); 102 (31.6); 104 (18.6). Known gas mixtures were made up in 1-liter bulbs and flowed through the hollow cathode; the electrical discharge sputters Ru atoms (or ions) which combine to some extent with oxygen before and during deposition at 14 K to give the solid matrix. The various oxides are expected to form by a chain of sequential reactions; the oxide distribution shifts from lower to higher oxides as the O_2/Ar ratio is increased and higher oxides form from lower by O atom capture stimulated by thermal annealing of the solid matrix. In various experiments, the $^{16}O/^{18}O$ ratio was varied from 0 to ∞, the total Ar/O_2 ratio was varied from 100 to 1000, and annealing temperatures up to 40 K were used to help in identifying the different oxide molecules.

III. RESULTS

Figure 1 shows a typical FTIR spectrum in the wavenumber region of interest of a matrix formed by sputtering. Absorption peaks (>960 cm^{-1}) are bands of O_3 isotopomers studied by Green and Ervin (*9*). The Ru oxide absorption spectra lie between 780 and 960 cm^{-1} and overlap considerably. Their complexity is due to the presence of both ^{16}O and ^{18}O in the Ar–O_2 gas mixture and to the presence of all seven naturally occurring stable isotopes of ruthenium. The metal isotopes produce a seven-line pattern

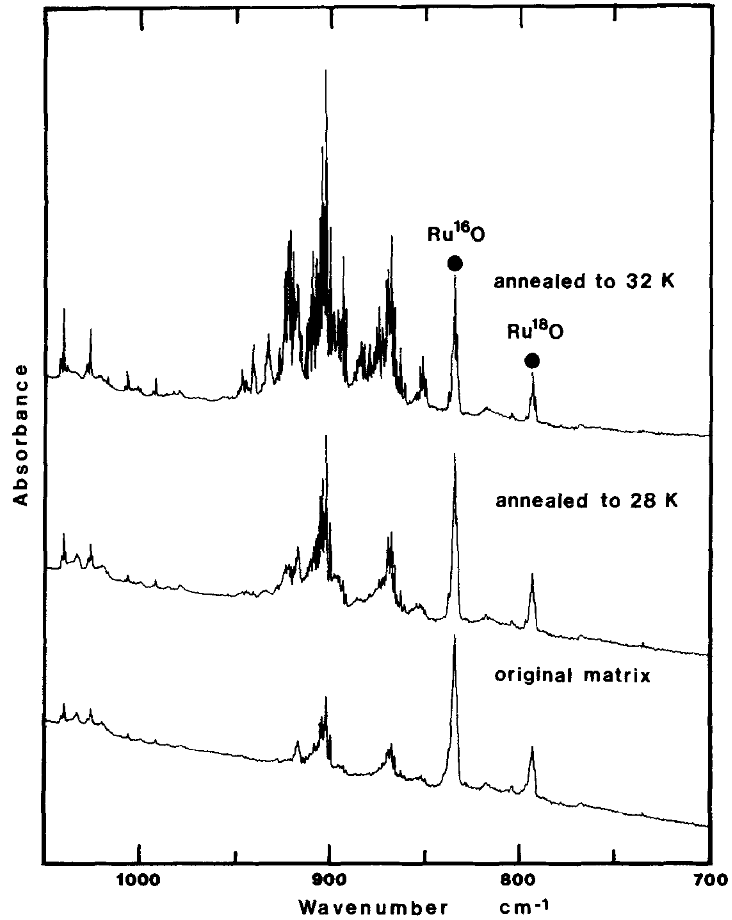

FIG. 1. Whole spectrum of ruthenium oxides as deposited at 14 K and subsequently annealed.

for each band. The original matrix was deposited and scanned at 14 K; the matrix was then allowed to warm to the indicated temperatures and immediately recooled to 14 K and scanned to give the annealed spectra shown. Note the substantial changes in the spectrum upon annealing that result from diffusion and further reaction of small species such as Ru or O atoms. One finds, from Wilson FG matrix calculations of frequencies which fit observed frequencies, that the Ru isotope separation ranges from about 0.1 to 1.0 cm^{-1} per unit change of Ru mass number. The intensity pattern of the seven Ru isotopes, which is determined by the relative abundances and is best seen in the spectrum of directly deposited RuO_4 in Fig. 6, is thus a helpful "fingerprint" for identifying any molecule containing a single Ru atom. Any species containing two Ru atoms with strong Ru–O or Ru–Ru bonds should show a much different and more complicated Ru isotope pattern. The mixtures of oxides formed in the sputtering experiments resulted from variation of $^{16}O/^{18}O$ isotope ratios from pure ^{16}O to (almost) pure ^{18}O, and a range of Ar/O_2 ratios from 130 to 1000. The different oxides were identified by the number of isotopomers, the dependence on O_2 concentrations and isotopic compositions in the argon gas, the behavior on annealing, and the quantitative agreement of the spectra with optimized *FG* matrix calculations from which reasonable molecular parameters (force constants, anharmonicity) are obtained. The calculations were carried out using programs originally written by J. H. Schachtschneider (*11*, *12*) and obtained from the Quantum Chemistry Program Exchange. The procedure followed was to identify the oxides successively in order of complexity, RuO, then RuO_2, then RuO_3, and, finally RuO_4. We will discuss the molecules separately in this order. Table I summarizes the observed and calculated isotopomer frequencies for ^{102}Ru and the average Ru isotope shifts per mass unit for all species observed.

IV. RuO

The two isotopomers, Ru^{16}O and Ru^{18}O, are easily recognized (see Figs. 1 and 2). The ratio of intensities is that of the O isotopes in the matrix. The identification of each isotopomer is facilitated by varying the O isotopic composition of the gas mixture. The two peaks are most prominent for small O_2/Ar ratios and tend to decrease in intensity on annealing as mentioned above. Even though the vibrational bands for the individual Ru isotopes are only partially resolved, the envelope shows the char-

TABLE I

Observed and Calculated Frequencies for Isotopomers of Ruthenium Oxides in Argon Matrices at 14 K

Isotopomer	Mode	ν(cm^{-1}) observed	ν(cm^{-1}) calculated	Average Ru isotope shift $\Delta\nu$/mass no (cm^{-1})^a	Bond angle and/or force constants^b
Ru^{16}O		834.4	834.4	0.58	5.698
Ru^{18}O		793.4	793.4	0.60	
Ru^{16}O$_2$	$\nu_1(A_1)$	926^c	926.7	0.10	$\theta = 149 \pm 2°$
	$\nu_3(B_1)$	902.2	902.5	1.04	
Ru^{16}O^{18}O	$\nu_1(A^1)$	916.9	916.2	0.40	
	$\nu_3(A^1)$	867.8	867.2	0.75	$f_r = 6.939 \pm 0.004$
					$f_{rr} = 0.994 \pm 0.005$
Ru^{18}O$_2$	$\nu_1(A_1)$		874.7	0.10	
	$\nu_3(B_1)$	862.9	862.7	1.09	
Ru^{16}O$_3$	$\nu_3(E)$	893.4	893.5	0.87	$\theta = 120 \pm {\sim}5°$
	$\nu_1(A_1)$		(950.1)	(0.08)	
Ru^{16}O$_2$^{18}O	$\nu_2(A_1)$	860^c	(860.1)	(0.87)	$f_r = 6.921$
	$\nu_4(B_1)$	893.4	893.5	0.87	$f_{rr} = 0.865$
	$\nu_1(A_1)$		(934.9)	(0.15)	$f_\alpha = 0.88$
Ru^{16}O^{18}O$_2$	$\nu_2(A_1)$	870.9	870.7	0.65	$f_{\alpha\alpha} = 0.06$
	$\nu_4(B_1)$	852.8	852.8	0.91	$f_{r\alpha} = f_{r\alpha} = 0.01$
Ru^{18}O$_3$	$\nu_3(E)$	852.8	852.8	0.91	d
Ru^{16}O$_4$	$\nu_3(T)$	920.8		0.9 ± 0.2	
I					
Ru^{18}O$_4$	$\nu_3(T)$	879.0	916.8	0.8 ± 0.2	$f_r = 6.75$
					$f_{rr} = 0.197$
Ru^{16}O$_4$	$\nu_3(T)$	916.5		1.0 ± 0.1	
II					
Ru^{18}O$_4$	$\nu_3(T)$	874.2	874.7	0.8 ± 0.1	

[a] numbers in parentheses indicate only calculated values
[b] force constants in mdyne/Å
[c] obscured by another band
[d] bending frequencies 301, 331 cm^{-1}

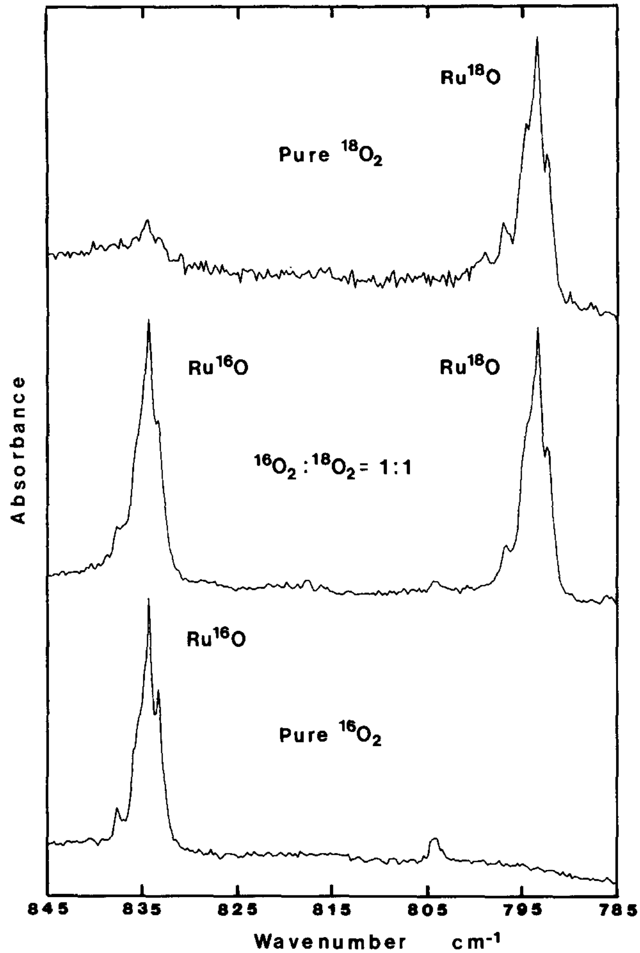

FIG. 2. Identification of RuO. A comparison of absorbance spectra for pure oxygen isotopes and a mixture of oxygen isotopes.

acteristic intensity pattern reflecting the natural isotopic abundances of ruthenium. The oxygen-18 substituted isotopomers appear in a clean region of the spectrum ($\nu = 793.44$ (± 0.04) cm^{-1} for $^{102}Ru^{18}O$) and are not overlapped; therefore, all of the isotopomers due to ruthenium are observable except for ^{98}Ru, which has a very low natural abundance. The characteristic isotope distribution pattern of ruthenium also is evident in the $Ru^{16}O$ bands around 834 cm^{-1} ($\nu = 834.44 \pm 0.04$ for $^{102}Ru^{16}O$), although it appears that these are partly overlapped by an unidentified compound of ruthenium. The determination of the fundamental vibration frequency and the anharmonicity for a diatomic molecule using the measured vibration bands of the isotopomers utilizes the following equations (*13*):

$$\rho = (\mu/\mu')^{1/2} = (\omega_e'/\omega_e) \quad (1)$$

$$\nu = \omega_e - 2\omega_e x_e \quad (2)$$

$$\nu' = \rho\omega_e - 2\rho^2\omega_e x_e \qquad (3)$$

$$\omega_e x_e = (\nu' - \rho\nu)/[2\rho(1 - \rho)]. \qquad (4)$$

ω_e is the fundamental vibrational frequency, $\omega_e x_e$ is the anharmonicity, ν is the observed frequency and μ is the reduced mass of the molecule. Here, the unprimed frequencies refer to ^{102}Ru^{16}O and the primed values refer to other isotopomers, i.e., ^{102}Ru^{18}O, ^{104}Ru^{16}O, etc. The vibrational energy, $G(v)$, for a diatomic molecule is then given by

$$G(v) = \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 + \cdots \qquad (5)$$

with v being the vibrational quantum number. The anharmonicity is first obtained from Eq. (4) using the observed frequencies and known isotopic masses for ^{102}Ru^{16}O and ^{102}Ru^{18}O. The value of ω_e is then calculated using either Eq. 2 or Eq. 3. Similarly, independent values of ω_e and $\omega_e x_e$ may then be obtained from other pairs of RuO isotopomers in the observed spectrum.

With the method of least squares, it is possible to use all the measured isotopomer frequencies of RuO to calculate the best values of ω_e'' and $\omega_e''x_e''$ for the molecule. However, the separations between ruthenium isotopomers are not always sufficiently resolved. We have, therefore, calculated the best values for the vibrational frequency and anharmonicity based on the unblended lines of ^{102,104}Ru^{16,18}O and used these as a basis for the calculated spectrum as shown in Fig. 3. It is seen that, using line widths adjusted to best reproduce the observed profiles, there is excellent agreement between the calculated and observed spectra. This not only helps confirm the identification of RuO as the carrier of these bands but shows the best values to be $\omega_e'' = 839.09 \pm 0.1$ cm^{-1} and $\omega_e''x_e'' = 1.8 \pm 0.05$ cm^{-1}. The mean of the calculated Ru isotope shifts is 0.60 ± 0.02 cm^{-1} per mass number.

Scullman and Thelin (*6*) reported $\omega_e'' = 863.5$ cm^{-1} for the "5526 Å" system observed in emission from a hollow cathode source. Rotational constants were reported for the ^{102}Ru^{16}O isotopomer. Isotope shifts also were measured for some isotopomers observed in the emission spectra. Using the Birge-Sponer extrapolation, Scullman and Thelin determined a dissociation energy in reasonable agreement with that (43×10^3 cm^{-1}) found using mass spectrometry (*4*).

Krauss and Stevens (*14*) have carried out extensive ab initio (MC-SCF) calculations on FeO and RuO. Their results suggest that RuO has a $^5\Delta$ ground electronic state with $\omega_e'' = 814$ cm^{-1}, $r = 1.74$ Å, and $\omega_e''x_e'' = 5.0$ cm^{-1}. Our value of ω_e'' shows a blue shift of 25 cm^{-1} from this calculated value and a red shift of 24.4 cm^{-1} (2.9%) from the gas phase value of Scullman and Thelin (*6*).

Krauss and Stevens (*14*) consider their calculated value to be in reasonable agreement with both the matrix-isolation result (~3% discrepancy) and the published gas phase value (~5.7% discrepancy). However, while such discrepancies between ab initio calculations of vibrational frequencies and experiment might be acceptable, better agreement should be expected between matrix-isolation and gas phase measurements.

Jacox (*15*) has reviewed the matrix shifts of ground state vibrational fundamentals and has shown that the matrix shifts nearly always are less than 2% with many less than 1% for diatomic metal oxides in solid argon. For example, the matrix shift is only −0.2% for FeO and 1.3% for MnO. Using 2% as an extreme limit, this suggests

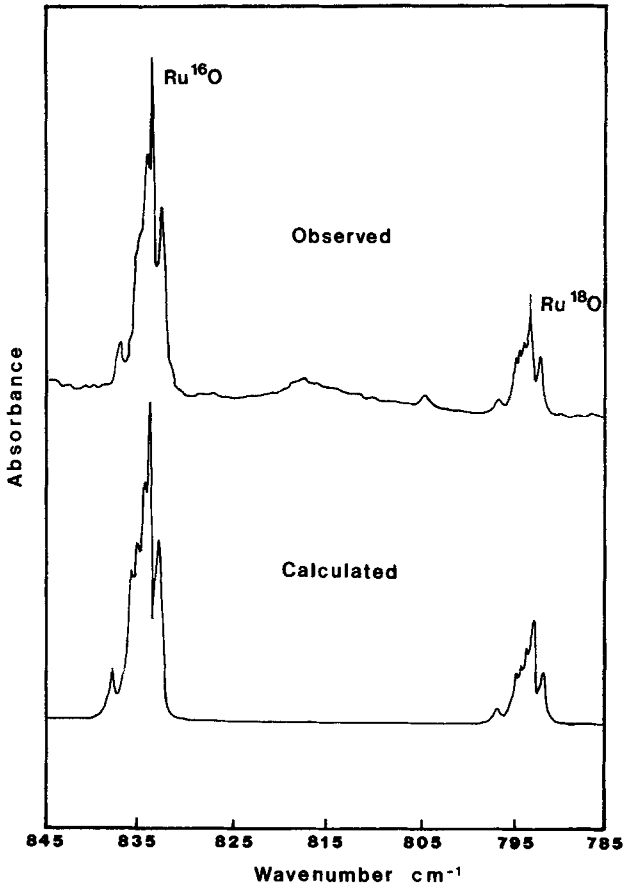

FIG. 3. Comparison of observed and calculated absorbance spectrum for RuO in an argon matrix prepared by sputtering a Ru cathode with an Ar: $^{16}O_2$:$^{18}O_2$ mixture. For the calculated spectrum, the parameters used are ^{16}O:^{18}O = 3:1; seven Ru isotopes in natural abundance; FWHM = 0.27 cm^{-1}; ω_e ($^{102}Ru^{16}O$) = 839.1 ± 1.0 cm^{-1}; $\omega_e x_e$ = 1.83 ± 0.5 cm^{-1}.

that the gas phase $\Delta G(\frac{1}{2})$ for RuO should be in the range 835 ± 17 cm^{-1}, i.e., between 818 and 852 cm^{-1}, based upon our matrix isolation measurements.

Using this criterion, the $\Delta G(\frac{1}{2})$ value of 819 cm^{-1} observed by Scullman and Thelin (*6*, *16*) as the difference between the band at 5532 Å and the one at 5807 Å makes the "5532 Å" system a slightly favored choice over the "5526 Å" system for belonging to the ground electronic state of the molecule. Of course, the spacing between the bands at 5532 Å and 5800 Å (834.1 cm^{-1}) (*6*) gives the best agreement of the "5532 Å" system to the electronic ground state of RuO, but requires a reassignment of the 5800 Å band to the "5532 Å" system rather than the "5526 Å" system [see (*6*)].

Based on the observation that matrix shifts of vibrational frequencies are typically less than 1% for diatomic metal oxides in solid neon (*12*), it would be worthwhile to repeat our experiments using neon instead of argon, but we were not able to do this with the cryogenic equipment available. It is clear, however, that more work also needs to be done on the gas phase spectrum of RuO. In this regard, some of us [see (*1*)] have succeeded in photographing the electronic spectrum of $RuO_{(g)}$ in absorption and a comparison of these spectra with the emission spectra of Scullman and Thelin (*6*) will be reported in a separate communication.

V. RuO_2

After eliminating RuO, one would expect, for the lower concentrations of O_2 in the sputtering gas, that the predominant absorptions would be the three ν_3 (asymmetric stretching) vibrations and, depending on molecular symmetry, the three ν_1 (symmetric stretching) vibrations belonging to the three possible isotopomers, $Ru^{16}O_2$, $Ru^{16}O^{18}O$, and $Ru^{18}O$, each of which would be expected to show the Ru isotope intensity pattern. Figure 4 illustrates their identification using different $^{18}O/^{16}O$ ratios. The individual Ru isotope peaks are well resolved and their relative intensities as well as the overall intensities of the three O-isotopomer patterns can be well reproduced from known Ru and O isotopic abundances, as shown by the calculated spectrum. Note that, since "pure" ^{18}O in the matrix always is or gets contaminated with a few percent of ^{16}O, one can see sometimes in the "pure" $Ru^{18}O_2$ spectrum the weaker $Ru^{16}O^{18}O$ band overlapping on the left as well as a small $Ru^{16}O_2$ peak.

From the various isotopomers with C_{2v} symmetry, one can show that the RuO_2 molecule is bent and derive values for the bond angle, θ, the harmonic frequency, ω_3, and the composite anharmonicity constant, x_3, where $\nu_3 = \omega_3 + x_3$. The background for such calculations is reviewed and discussed by Green and Ervin in (*9*). If we write ABA, $A'B'A'$, and $AB'A$ for three C_{2v} isotopomers, where $A = {}^{16}O$, $A' = {}^{18}O$, $B = {}^{102}Ru$, and B' = any other Ru isotope, one can directly calculate the upper and lower limits for the bond angle, θ, from the relations

$$\sin(\theta_{\text{upper}}/2) = [m_B(m_A - m_{A'}R_A)/2m_Am_{A'}(R_A - 1)]^{1/2} \tag{6}$$

$$\sin(\theta_{\text{lower}}/2) = [m_Bm_{B'}(1 - R_B)/2m_A(R_Bm_{B'} - m_B)]^{1/2}, \tag{7}$$

and where

$$R_A = [\nu_3(A'BA')/\nu_3(ABA)]^2 \quad \text{and} \quad R_B = [\nu_3(AB'A)/\nu_3(ABA)]^2, \tag{8}$$

where the ν_3's are the observed frequencies for the various isotopomers. For harmonic frequencies, the $\theta_{\text{upper}} = \theta_{\text{lower}} = \theta_{\text{true}}$. There are nine observed ν_3 frequencies which can be measured to a precision of $<0.1\ \text{cm}^{-1}$, i.e., Ru 104, 102, 101, 100, 99, combined with O 16 and 18 (omitting $^{99}Ru^{18}O_2$). For these frequencies one finds $\theta_{\text{upper}} = 165.9\ \{+2.6\ -2.2\}$ and $\theta_{\text{lower}} = 151.4\ \{+8.6\ -6.6\}$, the larger uncertainty being due to the smaller Ru isotope effect. In Ref. (*9*) general calculations suggest that the true angle should be close to the lower limit; also given is a procedure for obtaining θ_{true}, ω_3, and x_3 from a redundant set of ν_3's. For some arbitrarily chosen angle one can calculate ω_3 and x_3 from a least-squares fit of observed frequencies to the calculated frequencies $\nu_3(\text{calc}) = R^{1/2}\omega_3 + Rx_3$, where R is the analogous isotopic ratio for the G-matrix elements. A plot then of the standard deviation vs θ will be a parabola with a minimum at θ_{true}. This procedure gives $\theta_{\text{true}} = 149 \pm 2°$ and, for $^{102}Ru^{16}O_2$, $\omega_3 = 915.2 \pm 1.1\ \text{cm}^{-1}$, and $x_3 = -13.1 \pm 1.1\ \text{cm}^{-1}$. Using this angle, the values of $\nu_3(\text{calc})$ in Table I follow from *FG* matrix calculations for the stretching modes. The calculations also

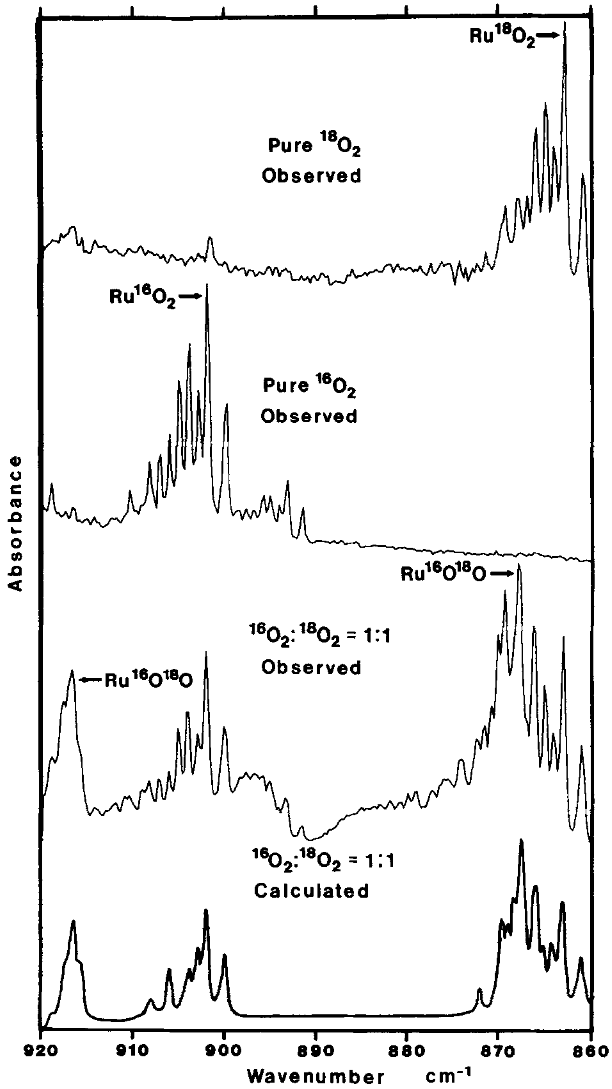

FIG. 4. Identification of RuO_2 and comparison of observed and calculated absorbance spectra. For the calculated spectrum, the parameters used are ^{16}O:^{18}O = 1:1; seven Ru isotopes in natural abundance; FWHM = 0.27 cm^{-1}; $\theta_{true} = 149 \pm 2°$; ω_3 ($^{102}Ru^{16}O_2$) = 915.2 ± 1.1 cm^{-1}; $x_3 = -13.1 \pm 1.1$.

yield ν_1 frequencies all of which are symmetry allowed, but only one of which, for $Ru^{16}O^{18}O$, is clearly seen and well reproduced. The best fit, given in Table I for all observed frequencies, corresponds to force constant values, $f_r = 6.939 \pm 0.004$ and $f_{rr} = 0.994 \pm 0.005$, both in mdyn/Å.

One might expect that the remaining two ν_1 absorptions would be weak since their intensities must go to zero for the linear limit. Very weak ^{102}Ru peaks can be seen within one wavenumber of the calculated values, 926.7 and 874.7 for the ^{16}O and ^{18}O isotopomers, respectively.

VI. RuO_3

Even at the highest workable O_2/Ar ratios and with annealing, RuO_3 is less concentrated in the matrix, and absorbs more weakly than RuO and RuO_2. Also the spectra of the four isotopomers tend to overlap with each other and with the RuO_2 spectra. Nevertheless, using pure $^{16}O_2$ and $^{18}O_2$ and varying the concentrations and annealing treatments as before, one can identify $Ru\,^{16}O_3$ and $Ru\,^{18}O_3$ as shown in Fig. 5 and estimate upper and lower limits for the angle, assuming all three are equal (see (*8*)). This need not be the case (*17*) but does turn out to give the best quantitative fit of the observed frequencies. The average of the two limits is around 119° with a large uncertainty and the best calculated fit gives an angle of 120°. Assuming D_{3h} symmetry, the ν_3 (E) stretching frequencies for the homogeneous molecules (HMs) and for all Ru isotopes can be fit quite closely, as shown in Fig. 5 and in Table I. We cannot,

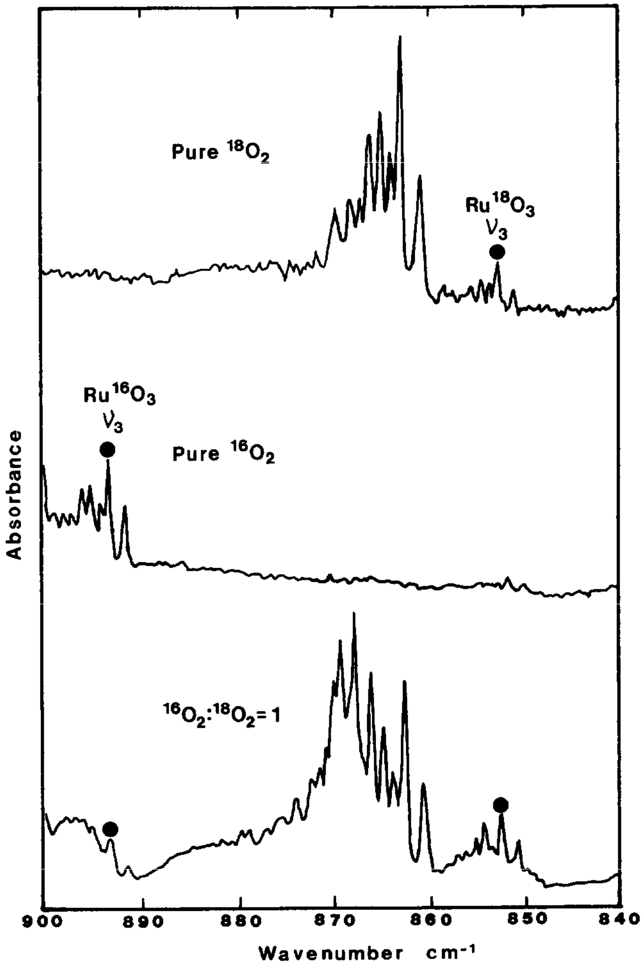

FIG. 5. Identification of RuO_3. A comparison of RuO_3 absorbance spectra for pure oxygen isotopes and a mixture of oxygen isotopes.

however, expect to make a more accurate estimate of the bond angle taking into account anharmonicity as for RuO_2 since, for RuO_3 (D_{3h}), the stretching and bending E modes will mix somewhat, and we have not observed the lower-frequency bending modes in this study. Furthermore, if only stretches are considered, a single parameter, $f_r - f_{rr}$, determines the E frequencies for the HMs and thus leaves the individual force constants undetermined, as can be seen in Table (3) of Ref. (*8*), where the stretching vibrational analysis is shown. Also shown is that for the two mixed isotopomers, the ν_4 (B) frequencies are identical to the ν_3 (E) frequencies for the HMs. If one carries out a full vibrational analysis (including bending modes) and adjusts the angular constant values to give bending frequencies around 300 cm^{-1} (as found for gaseous RuO_4 (*18*, *19*)) and the remaining force constants to give an equally good fit of ν_3 for the HMs, one finds that the ν_4 (B) $\leftrightarrow$ ν_3 (E) degeneracy and the f_r indeterminancy still remain. Because of the overlapping and congestion, it is hard to find the ν_2 (A_1) and probably not possible to find the ν_1 (A_1) frequencies for the mixed isotopomers. One possibility for ν_2 (A_1) of $^{102}Ru^{16}O^{18}O_2$ is shown in Table I. The 870.9 cm^{-1} ^{102}Ru peak is almost always seen and in one run six observed peaks at this location agree with the calculated Ru isotope shift shown in the table. The predicted peak for $^{102}Ru^{16}O_2{}^{18}O$ at 860 cm^{-1} lies under another peak and cannot be identified. Considering that anharmonicity is neglected, the calculated frequencies shown are in excellent

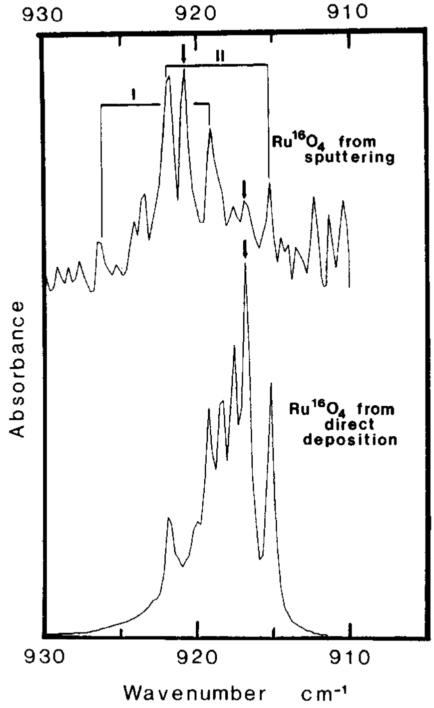

FIG. 6. The ν_3 vibration for $Ru^{16}O_4$ from sputtering spectra showing a mixture of two forms and a direct deposition spectrum showing the presence of only one form (see text). The arrows indicate the ^{102}Ru isotope in each isotopomer.

agreement with the observed ones. The calculation shows that the ν_1 (A_1) peaks have such a small Ru isotope shift that they would appear as a single peak; in addition one would expect their intensities to be quite small. We have been unable to identify such bands.

VII. RuO_4

We have observed the absorption spectrum of an RuO_4–Ar matrix by direct deposition of the gas mixture. This is discussed in a separate communication (*10*), which concludes that all experimental frequencies and intensities for all 35 possible isotopomers presuppose a regular tetrahedral structure, as has been established for gaseous RuO_4 (*18, 19*). Relative to the gas the matrix frequencies show a red shift of about 4 cm^{-1} (<0.5%). In the presently discussed sputtering experiments, $Ru^{16}O_4$ and $Ru^{18}O_4$ absorptions can be identified in cases with high O_2/Ar concentrations and annealing (see Fig. 6). However, there appear to be two sets of frequencies (see Table I), one present in minor amounts, identical with that from the direct deposition (II in Table I and Fig. 6) and another, much more intense (I in Table I and Fig. 6), blue shifted by again 4 cm^{-1} to be very close to the gas phase spectrum, a result which is surely coincidental. We suggest that II represents the equilibrium tetrahedral molecule and that I represents a slightly perturbed state of RuO_4, where the perturbation is caused by an asymmetry in the matrix site possibly due to adjacent species other than Ar, such as O_2 or O. In the sputtering case, when RuO_4 is formed (say by RuO_3 + O or RuO_2 + O_2 during annealing) there surely can be excess O_2 and O remaining in the matrix.

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The authors are grateful to Gilbert J. Mains for consenting to do ab initio calculations relating to the structures of RuO_2 and RuO_3. It is interesting to note that these calculations predicted that RuO_2 should be bent in the triplet state. Since RuO appears to have a ground state of $X^5\Delta$ (*6, 13*), this, combined with $O(^3P)$, could give RuO_2 with a triplet (but not a singlet) ground state (*20*). Calculations for RuO_3 suggested the possibility of a C_{2v} structure (somewhate unequal bonds and angles) as opposed to D_{3h}. Three of the authors (Jack G. Kay, George L. Zimmerman, Karen Duca) express their appreciation to the Division of Educational Programs and the Chemical Technology Division of Argonne National Laboratory, which is run for the Department of Energy under Contract W-31-109-Eng-38, for partial support during the course of this work. They also thank the chemistry departments of Bryn Mawr College and Drexel University and Stephen Russo of the Bryn Mawr chemistry department for their support and help.

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