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Laser-induced fluorescence and dispersed fluorescence spectroscopy, isotopic studies, and lifetime measurements for rhodium monoxide

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Abstract

RhO molecules have been generated from laser-ablated rhodium atoms and $^{16}O_2$ or $^{18}O_2$ and studied spectroscopically. Thirty LIF band features in the 500–650 nm region have been examined. Dispersed fluorescence and excited state lifetime data have been recorded. Measurements on vibrational levels $v = 0$ to 5 of the molecular ground state give $\omega_e = 807$ cm^{-1} and $\omega_e x_e = 5$ cm^{-1}. Excited state vibrational parameters have been estimated. Evidence is found for low-lying electronic states at 3744, 5980 and 6477 cm^{-1}.
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1. Introduction

Rhodium monoxide is one of the least well characterized of the transition metal monoxides. Laser-induced fluorescence (LIF) studies of a rhodium metal + O$_2$/He plasma have revealed a rich and complex array of vibronic bands in the 500–650 nm region and, in a recent publication [1], we have shown that the lowest energy bands in this spectrum belong to two electronic transitions in the RhO radical, of $^2\Pi_r$–$X^4\Sigma^-$ type. We refer to these transitions as [15.8]$^2\Pi$–$X^4\Sigma^-$ and [16.0]$^2\Pi$–$X^4\Sigma^-$

since their respective sub-band origins lie at 15 667, 15 976 and 15 874, 16 167 cm^{-1}. In the present work we have used ^{16}O/^{18}O isotopic substitution, excited state lifetime measurements, and dispersed fluorescence (DF) spectroscopy to classify more band features, obtain RhO vibrational information, and probe for additional electronic states, which may be low-lying in energy.

There is some information available on RhO from other sources. Citra and Andrews [2] examined the infrared absorption spectra of laser-ablated rhodium atoms co-deposited with oxygen in an argon matrix at 7–8 K and assigned vibrational features at 799.0 and 759.8 cm^{-1} to Rh^{16}O and Rh^{18}O, respectively. Thermodynamic data have been used by Chen and Armentrout [3] to estimate the Rh–O ground state bond dissociation energy, D_0, at 33 800 cm^{-1} (4.19 ± 0.43 eV), and anion

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photoelectron spectroscopy [4] on RhO indicated that electronic levels exist at $\sim$1600, 3800, 5700 and 8100 cm^{-1} and estimated a ground state vibrational interval of 730 ± 80 cm^{-1}.

2. Experimental method

The experimental apparatus consisted of a standard laser vaporization molecular beam source, two pulsed laser systems and the necessary hardware and software for LIF detection. Details have been given in a previous publication [5]. Briefly, a rotating and translating rhodium rod (5-mm diameter $\times$ 30-mm, 99.9% purity, Goodfellow) was used together with a stream of helium, doped $\sim$5% with $^{16}O_2$ and/or $^{18}O_2$ (98%, Cambridge Isotope Labs). A Nd:YAG pumped dye laser (Lumonics HY600 and HD 300 with DCM, Rhodamine 590, 610 and 640, and Kiton Red 620 dyes) gave excitation in the 500–650 nm range. Fluorescence was collected through a Jobin-Yvon H20 monochromator and converted to an electrical signal by a Hamamatsu R106UH photomultiplier tube. Ex situ wavelength calibration was obtained via optogalvanic signals from an Fe/Ne hollow cathode lamp. DF was generally recorded by tuning the excitation laser to coincide with a strong feature at the center of a given LIF band. We estimate the uncertainty in our DF spectral intervals to be less than 15 cm^{-1}. To determine excited state lifetimes, intensity–decay profiles were obtained by tuning the probe laser to a strong rovibronic transition. Upto 500 probe laser shots were averaged for each excited state measurement and three to five such measurements were averaged to give a band-averaged lifetime. The precision for a given τ measurement was typically ± 5 ns. However, the standard deviation of a band-averaged lifetime was considerably greater (see footnote to Table 3).

3. Results

3.1. Isotopic studies

About 30 LIF band features from Rh + O$_2$ are present between 500 and 650 nm. The 555–640 nm region, which contains the stronger bands, was subsequently surveyed using $^{18}O_2$ in place of $^{16}O_2$. These isotopic substitution experiments confirmed that all of the observed band features belong to RhO: no spectra attributable to impurities were found. The measured Rh^{16}O–Rh^{18}O energy shifts have enabled vibrational progressions to be assigned in the upper state manifolds. The data are summarized in Table 1. That the shifts are somewhat erratic with vibrational quantum number may be attributed to slight differences in perturbational shifts in the two isotopomers.

3.2. Dispersed fluorescence spectra

Dispersed fluorescence spectra were obtained from excitation to the majority of the Rh^{16}O vibronic levels found in the LIF studies. In all instances emission is seen to the X$^4\Sigma^-$ ($v = 0$) level (i.e., at the probe laser frequency) and to a level lying at 797 cm^{-1} above the ground level, which is clearly the X$^4\Sigma^-$ ($v = 1$) level. In many instances additional emission is seen to additional ground vibrational levels and to other levels. Four examples of DF spectra are shown in Fig. 1. Table 2 lists the positions and relative intensities of the observed DF features. Similar data were collected for the Rh^{18}O isotopomer but these spectra were weaker and of inferior quality.

The DF intensity patterns are governed by the Franck–Condon effect. The spectrum in Fig. 1c is representative of the emission seen from the $v = 0$ levels of the [15.8]$^2\Pi$ and [16.0]$^2\Pi$ states: the 0–0 transition carries most of the intensity. This is expected where the excited state potential energy curves have shapes and r_e minima similar to the ground state. The spectrum in Fig. 1a is an example of emission from a $v' = 1$ level. In some cases, for example Fig. 1d, the vibrational pattern in the ground state can be mapped to $v = 5$. There are three levels, seen at $T = 3744$, 5980 and 6477 cm^{-1}, which do not fit into the ground state vibrational progression and must therefore belong to other low-lying electronic states. Furthermore DF spectra following excitation near 588.7 and 553.7 nm show additional weak features (see footnotes to Table 2). These features can be seen in Figs. 1a and b accompanying the stronger peaks

Table 1
Band centers and vibronic assignments in the visible spectrum of $Rh^{16}O$ and $Rh^{18}O$ from low-resolution observations

$Rh^{16}O$		$Rh^{18}O$		Shift	Assignment
nm	cm^{-1}	nm	cm^{-1}	cm^{-1}	
649.9	15 387	–	–	–	$[16.0]^2\Pi_{3/2}$–$X^4\Sigma^-$ (0,1)
638.2	15 668	638.2	15 668	–	$[15.8]^2\Pi_{1/2}$–$X^4\Sigma^-$ (0,0)
629.7	15 877	629.7	15 877	–	$[16.0]^2\Pi_{1/2}$–$X^4\Sigma^-$ (0,0)
625.5	15 978	–	–	–	$[15.8]^2\Pi_{3/2}$–$X^4\Sigma^-$ (0,0)
618.3	16 170	618.3	16 170	–	$[16.0]^2\Pi_{3/2}$–$X^4\Sigma^-$ (0,0)
618.0	16 177	–	–	–	$[16.0]^2\Pi_{3/2}$–$X^4\Sigma^-$ (1,1)
607.9	16 447	608.9	16 427	20	$[15.8]^2\Pi_{1/2}$–$X^4\Sigma^-$ (1,0)
598.1	16 720	599.4	16 684	36	$[16.0]^2\Pi_{1/2}$–$X^4\Sigma^-$ (1,0)
594.3	16 827	595.7	16 788	40	$[15.8]^2\Pi_{3/2}$–$X^4\Sigma^-$ (1,0)
588.7	16 986	590.0	16 948	38	$[16.0]^2\Pi_{3/2}$–$X^4\Sigma^-$ (1,0)
584.1	17 120	586.1	17 062	58	$[15.8]^2\Pi_{1/2}$–$X^4\Sigma^-$ (2,0)
578.9	17 274	579.2	17 265	9	$[15.8]^2\Pi_{1/2}$–$X^4\Sigma^-$ (3,1)
573.5	17 438	575.1	17 389	49	$[16.0]^2\Pi_{1/2}$–$X^4\Sigma^-$ (2,0)
569.3	17 565	571.6	17 495	70	$[15.8]^2\Pi_{3/2}$–$X^4\Sigma^-$ (2,0)
561.9	17 797	564.3	17 721	76	$[16.0]^2\Pi_{3/2}$–$X^4\Sigma^-$ (2,0)
554.7	18 027	–	–	–	Weak
553.3	18 074	555.8	17 993	81	$[15.8]^2\Pi_{1/2}$–$X^4\Sigma^-$ (3,0)
546.1	18 312				$[16.0]^2\Pi_{1/2}$–$X^4\Sigma^-$ (3,0)
544.6	18 362				$[15.8]^2\Pi_{3/2}$–$X^4\Sigma^-$ (3,0)
542.8	18 424				Weak
541.7	18 461				Weak
539.8	18 526				$[16.0]^2\Pi_{3/2}$–$X^4\Sigma^-$ (3,0)
537.3	18 612				
534.6	18 705				
526.5	18 992				
524.5	19 067				
521.8	19 165				
519.7	19 240				
518.0	19 304				

and to higher displacement energies. We do not have a ready explanation for these latter observations. The measured intervals appear to be different in the two examples and seem too small to be attributed to low-lying levels. It may be significant that these are the only bands in the LIF spectrum where rotational perturbations are clearly evident. Finally, there are two instances (Table 2) where a weak anti-Stokes signal is found. Their excitation arises from $v = 1$ in the $X^4\Sigma^-$ state.

3.3. Excited state lifetimes

Some excited state lifetime data have been measured and are reported in Table 3. The long-lived excited states reinforce the conclusion of the rotational analysis [1] that the electronic transitions giving rise to the RhO visible spectrum are spin-forbidden. The lifetimes of the four $v = 0$ excited states are different but correlate well with observed relative intensities in the LIF spectra. The 637.8, 625.9 $[15.8]^2\Pi$–$X^4\Sigma^-$ pair of (0,0) subbands are markedly less intense and longer lived than the 629.9, 618.0 $[16.0]^2\Pi$–$X^4\Sigma^-$ (0,0) pair and within each pair it is the higher energy, $^2\Pi_{3/2}$–$X^4\Sigma^-$ subband that is the stronger.

4. Discussion

The observed $X^4\Sigma^-$ vibrational level data (±15 cm^{-1}) from the $Rh^{16}O$ DF spectra yield the relation [2] $G(v)$ $cm^{-1} = 805 \pm 0.6(v + 1/2)-$
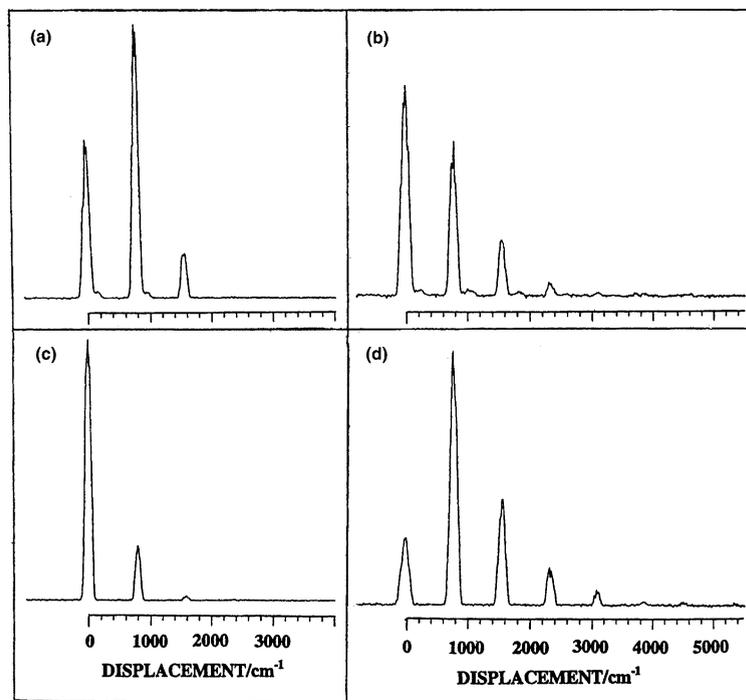
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[2] Uncertainties represent 1σ.

Fig. 1. Dispersed fluorescence spectra from selected excited vibronic levels of Rh^{16}O. The excitation wavelengths (in nm) were: (a) 588.7; (b) 553.7; (c) 637.8; (d) 535.8.

$5 \pm 0.1(v + 1/2)^2$, in excellent and possibly fortuitously good agreement with the value for the vibrational interval $\Delta G(1/2) = 799.0$ cm^{-1} observed in matrix isolation studies [2]. A simple Birge–Sponer extrapolation gives an upper estimate for the RhO ground state dissociation energy of $\omega_e^2/4\omega_e x_e = 36\,000$ cm^{-1}. Chen and Armentrout's estimate [3] from thermochemistry is $\sim 34\,000$ cm^{-1}.

For Rh^{18}O, where the corresponding DF data are sparse and less reliable (± 10 cm^{-1}) we find vibrational levels at 749, 1505, and 2247 cm^{-1}, as against a matrix $\Delta G(1/2)$ value of 759.8 cm^{-1}.

In the upper states vibrational progressions are irregular (Fig. 2). Nevertheless, rough estimates of vibrational parameters can be made. Data from the four progressions ($v = 0$–3) were fitted to

$$T = T_e + \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2$$

using a non-linear sum-of-squared differences procedure, together with the added constraint that

the potential energy curves for the ground and the [15.8]$^2\Pi$ and [16.0]$^2\Pi$ states share a common dissociation limit. The summary of the results, given in Table 4, shows that the vibrational parameters in the upper states are similar to those in the ground state.

Photoelectron spectroscopy experiments on the RhO$^-$ anion [4] gave evidence for low-lying states of the neutral species at $T = 1600, 3800, 5700$ and 8100 ± 100 cm^{-1}. It is of interest to compare these observations with the DF data obtained in the present study. We find no evidence in our spectra to indicate the presence of a level near 1600 cm^{-1} other than the X$^4\Sigma^-$, $v = 2$ level at 1584 cm^{-1}. The 1600 cm^{-1} level was attributed to the $^4\Sigma^-_{1/2}$ component of the ground state in Hund's case (a) model. This is incorrect. Rotational analysis [1] has confirmed that the RhO ground state conforms closely to Hund's case (b). Li and Wang's level at 3800 cm^{-1} can clearly be identified with the 3744 cm^{-1} DF level. It appears only weakly in the DF spectra and we cannot draw any conclusions re

Table 2
Relative intensities in dispersed fluorescence spectra of $Rh^{16}O$

Emission to:		Wavelength excited (nm)									
		638.2	629.7	625.5	618.3	607.9	598.1	594.3	588.7[a]	584.1	573.5
X, $v = 0$	$T = 0$	100	100	100	100	100	30	75	50	100	100
X, $v = 1$	797	20	10	7	5	5	100	100	100	50	30
X, $v = 2$	1584	3				2	25	10	15	5	12
X, $v = 3$	2362					3	2	5		1	3
X, $v = 4$	3131					1		2		2	5
X, $v = 5$	3891									2	2
Level at	3744										2

Emission to:		569.3	561.9	553.3[b]	546.1	544.6	543.4	542.8	541.7	540.4	539.8
X, $v = 0$	$T = 0$	15	20	100	100	100	100	100	100	100	100
X, $v = 1$	797	100	100	75	10	40	25	65	80	55	25
X, $v = 2$	1584	100	75	30	20	80	5	25	30	15	3
X, $v = 3$	2362	40	25	7	10	25		15	20	20	
X, $v = 4$	3131			2	10	25		10	10	8	
X, $v = 5$	3891			2					<1		
Level at	3744			2				4	2		

Emission to:		538.9	537.3	534.6	526.5	524.5	521.8	518.0	649.9[c]	616.9[c]
X, $v = 0$	$T = 0$	75	15	40	65	100	40	45	100	25
X, $v = 1$	797	100	55	100	100	55	100	100	25	100
X, $v = 2$	1584	35	100	70	4	90	25	40	5	10
X, $v = 3$	2362	50	65	35	7	25	9	5		
X, $v = 4$	3131	25	40	20			4			
X, $v = 5$	3891			2			4			
Level at	3744									
Level at	5980							1		
Level at	6477							5		

[a] Excitation within the 588.7 nm band gives additional weak features at dispersed fluorescence displacements of 180 and 968 cm^{-1} (see Fig. 1a).

[b] Excitation within the 553.3 nm band gives additional weak features at dispersed fluorescence displacements of 212, 1051 and 1852 cm^{-1} (see Fig. 1b).

[c] Excitations within LIF bands at 649.9 and 616.9 nm show an anti-Stokes dispersed fluorescence line at $v_{probelaser} + 797 cm^{-1}$ confirming that these bands arise from the $v = 1$ level in the ground state.

Table 3
Radiative lifetimes[a] in excited vibronic states of $Rh^{16}O$

Band excited (nm)	τ (ns)	Band excited (nm)	τ (ns)	Band excited (nm)	τ (ns)
638.2	1600	598.1	1000	561.9	450
629.7	900	594.3	800	553.3	1200
625.5	1000	588.7	450	544.6	1200
618.3	500	573.5	1700	542.8	1300
607.9	1700	569.3	600		

[a] For $\tau < 1000$ ns the estimated error is ± 100 ns; for $\tau > 1000$ ns the estimated error is ± 200 ns.

its electronic assignment. The prominent photoelectron peak at 5700 cm^{-1} has no obvious counterpart in the DF spectra. We do, however, see evidence for emission to levels at 5980 (vw) and 6477 (w) cm^{-1}. It is relevant to note that selection rules governing the transitions in the photoelec-
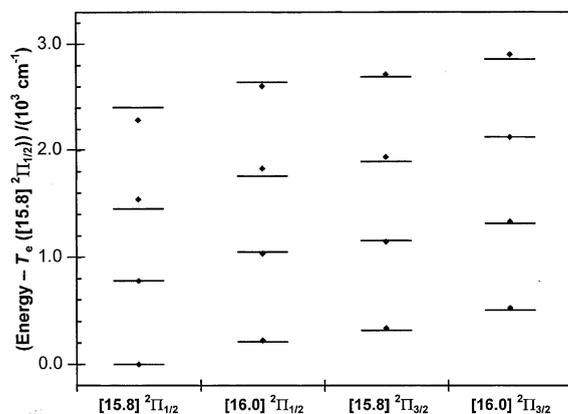
Fig. 2. Energy level diagram of RhO excited vibronic states. Horizontal lines indicate observed positions; ◆ indicate positions calculated from parameters in Table 4.

Table 4
Vibrational parameters[a] for the ground $^4\Sigma^-$, and excited [15.8]$^2\Pi$ and [16.0]$^2\Pi$ states of Rh^{16}O (in cm^{-1}).

State	T_e[b]	ω_e	$\omega_e x_e$	D_e
X$^4\Sigma^-$	0	805	4.5	35 785
[15.8]$^2\Pi_{1/2}$	15 673	785	7.7	20 120
[15.8]$^2\Pi_{3/2}$	15 994	818	8.4	19 830
[16.0]$^2\Pi_{1/2}$	15 883	817	8.4	19 940
[16.0]$^2\Pi_{3/2}$	16 162	831	8.8	19 625

[a] Estimated errors for upper state parameters are: $T_e(\pm9)$; $\omega_e(\pm10)$; $\omega_e x_e(\pm2)$.
[b] Deperturbed values.

tron experiments and the dispersed fluorescence experiments may differ. Until electronic assignments are established for the emitting levels, it is idle to speculate on the nature of these 5980 and 6477 cm^{-1} levels.

5. Conclusions

Measurements have been made which confirm that the visible electronic transition in the RhO molecule is a spin-forbidden one. Ground state vibrational levels up to $v = 5$ have been seen and indicate that the vibrational frequency in an argon matrix and in the gas phase are very similar. Evidence in support of an electronic state at $\sim$3700 cm^{-1} as proposed by Li and Wang [4] is found. In addition, dispersed fluorescence experiments suggest two new low-lying electronic states near 6000 and 6500 cm^{-1}.

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