

# Raman spectra of rhodium trimers in argon matrices

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(Received 22 May 2000; accepted 4 August 2000)

Resonance Raman spectra of rhodium trimers ( $\text{Rh}_3$ ) in argon matrices have been obtained for the first time. Our samples are prepared by neutralizing a mass-filtered beam of trimer ions. Although the absorption spectrum of our optically thin samples failed to show any obvious transitions, a rich Raman spectrum was found for laser excitation wavelengths between 545 nm and 593 nm. Three fundamentals, corresponding to normal modes of a bent ( $C_{2v}$ ) molecule can be assigned with up to four overtones in the symmetric stretch. Using standard techniques, we obtained for this mode  $\omega_e = 322.4(6) \text{ cm}^{-1}$ , with  $\omega_e x_e = 0.49(10) \text{ cm}^{-1}$ . The resulting stretching force constant is  $k_e = 2.10 \pm 0.01 \text{ mdyne/\AA}$ . Assuming a Morse potential governs the symmetric stretching normal coordinate, we obtain an atomization energy of  $D_e = 6.6 \pm 1.4 \text{ eV}$ . The asymmetric stretch and bend are found at  $259 \text{ cm}^{-1}$  and  $247.9(8) \text{ cm}^{-1}$ , respectively. A line at  $400 \text{ cm}^{-1}$  is observed, which does not fit the normal mode scheme of the ground state. This is assigned as the origin of a low lying electronic state. © 2000 American Institute of Physics. [S0021-9606(00)00941-7]

## I. INTRODUCTION

Although rhodium is quite important as a catalyst in many processes, there is little experimental information about the properties of small rhodium clusters.<sup>1</sup> The Raman spectra of rhodium dimers in argon matrices have been obtained in our laboratory<sup>2</sup> in 1997. Ozin and Hanlan<sup>3</sup> obtained optical spectra of various rhodium clusters. The only other available experimental information on rhodium trimer is obtained from ESR by Van Zee *et al.*<sup>4</sup> They concluded that rhodium trimer has an equilateral triangle structure ( $D_{3h}$  symmetry) with the unpaired spins essentially in non-bonding orbitals involving atomic  $d\delta$  atomic orbitals. Their result was in agreement with the theoretical calculations of Dai and Balasubramanian.<sup>5</sup> Das and Balasubramanian<sup>6</sup> calculated the potential energy surface of eight low-lying electronic states of  $\text{Rh}_3$ . Chien, Blaisten-Barojas, and Pederson have carried out density functional calculations on small Rh clusters with similar conclusion.<sup>7</sup>

In this paper we report on the observation of resonance Raman spectra of  $\text{Rh}_3$  in an argon matrix. Our samples are prepared by neutralizing a mass selected beam of trimer ions. Although the absorption spectrum (scattering depletion spectrum) failed to show any obvious absorption transitions from 200 nm to 850 nm, a rich Raman spectrum was found between 545 nm and 593 nm. Three fundamentals, corresponding to normal modes of a bent ( $C_{2v}$ ) molecule can be assigned, with up to four overtones in the symmetric stretch ( $a_1$ ). We obtained for this mode  $\omega_e = 322.4(6) \text{ cm}^{-1}$ , with  $\omega_e x_e = 0.49(10) \text{ cm}^{-1}$ , leading to  $k_e = 2.10 \pm 0.01 \text{ mdyne/\AA}$  and an atomization energy of  $6.6 \pm 1.4 \text{ eV}$ . The asymmetric stretch and bend are found at  $259 \text{ cm}^{-1}$  and  $247.9 \text{ cm}^{-1}$ , respectively. A line at  $400 \text{ cm}^{-1}$  is assigned as the origin of a low lying excited state.

## II. EXPERIMENT

The City College of New York (CCNY) metal cluster deposition source has been described in previous publications.<sup>8,9,10</sup> Briefly, an intense (typically 15 mA at 25 keV) argon ion beam from a CORDIS ion source sputters on a water cooled rhodium target (Alfa, 99.9% REO) maintained at around 300 V. Secondary ions are extracted with a modified Colutron model 200-B lens system and then mass selected using a Wien filter (C\*olutron 600-B) in conjunction with an approximately 175 mm free drift distance and a 6.5 mm diam aperture. After mass selection, the ion beam is bent by  $10^\circ$  using two electric plates to eliminate neutrals and then guided and focused to the deposition region by two einzel-like lenses.

Rhodium trimer ions were codeposited with argon and electrons (generated from a heated tungsten filament) on a polished  $\text{CaF}_2$  substrate ( $\sim 16 \text{ K}$ ). Matrices were grown at  $\sim 5 \mu\text{m/h}$  with an Ar:metal dilution ratio of approximately  $10^4:1$ . The deposition region was surrounded by a "Faraday Cage" whose potential with respect to the sputtering target controls the kinetic energy (20 eV in this experiment) of deposited ions. Ion currents under "soft landing" conditions were approximately  $\text{Rh}^+$  (120 nA),  $\text{Rh}_2^+$  (12 nA), and  $\text{Rh}_3^+$  (12 nA). The rhodium trimer sample was prepared with about 6 h deposition, totally 60 nA h.

Matrix samples were interrogated *in situ* using both absorption and Raman spectroscopy. As previously described,<sup>8,9,10</sup> the technique termed SDS was applied, but no obvious absorption feature could be possibly assigned to rhodium trimers.

The Raman spectra were measured by exciting the sample with the visible light (457.9 nm–514.5 nm) of an argon ion laser (Spectra-Physics model 2045), tunable dye laser, and Ti-Sapphire laser. The scattered light was collected at  $90^\circ$  and focused into a Triplemate Spectrometer

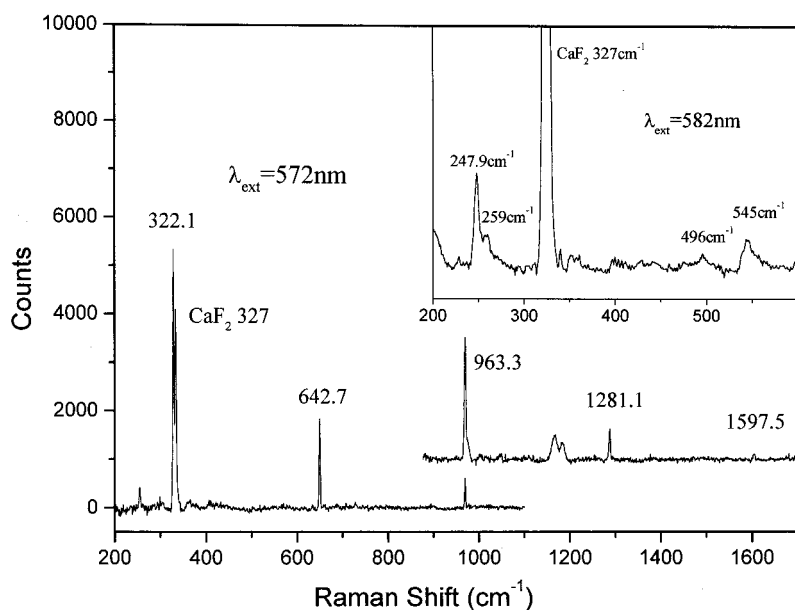


FIG. 1. Raman spectrum of rhodium trimers in argon matrices excited at 572 nm. A fraction of another Raman spectrum excited at 582 nm is shown as insert.

(Spex 1877E, 0.6 m). The scattered light was detected with a liquid nitrogen cooled CCD system (Spectrum One and CCD30). The Raman shifts of  $\text{Rh}_3$  were calibrated with the nonresonance Raman line of the  $\text{CaF}_2$  (substrate) at  $327\text{ cm}^{-1}$ .

### III. SPECTRA AND ANALYSIS

In Fig. 1 we show a typical resonance Raman spectrum of rhodium trimers in argon matrices. Most of the stronger lines are observed over a range of excitation of 540–590 nm, while a few weaker lines show up only in still narrower segments of the excitation range. A summary of the spectral observations is presented in Table I. A consistent progression of five lines in  $322\text{ cm}^{-1}$  is observed throughout the range, and this is assigned as the totally symmetric stretch  $\nu_1$ . If the molecule were in an equilateral triangular geometry ( $D_{3h}$ ) we would expect only one more vibration, a doubly degenerate ( $e'$ ) mode at  $\nu_1/\sqrt{2}$  (Ref. 11) or around  $228\text{ cm}^{-1}$ . Instead we see two lines at  $259\text{ cm}^{-1}$  and  $247.9\text{ cm}^{-1}$ . This is characteristic of a bent ( $C_{2v}$ ) molecule and we may assign these to the  $\nu_2(b_1)$  asymmetric stretch and the  $\nu_3(a_1)$  bend, respectively. The  $259\text{ cm}^{-1}$  is somewhat weaker than the

$247.9\text{ cm}^{-1}$  line, and we only tentatively assign the still weaker feature at  $545\text{ cm}^{-1}$  as an overtone  $2\nu_2$ , indicating considerable anharmonicity, if correct. Alternatively, this could represent a low lying electronic state, since its excitation profile differs somewhat from that of the symmetric stretch. More certain is the assignment of the line at  $496\text{ cm}^{-1}$  to the first overtone ( $2\nu_3$ ) of the bending mode. The only remaining line is that at  $400\text{ cm}^{-1}$  which is observed in the range 582–576 nm, centered around 578 nm. It is narrow and moderately intense, but does not fit any scheme of ground state vibrations. All transition metal clusters are expected to have numerous low lying electronic states due to open  $d$ -shell atomic configurations. It is not unreasonable to assign this line as the origin of such a state and we designate it is the  $A$  state to distinguish it from the  $X$  ground state.

The long progression (see Table I, The Raman shifts were averaged over 30 spectra at different wavelengths and the standard deviation is included) the symmetric stretch ( $\nu_1$ ) vibration may be fit by standard techniques,<sup>12</sup> giving  $\omega_e = 322.4(6)\text{ cm}^{-1}$ , with  $\omega_e x_e = 0.49(10)\text{ cm}^{-1}$ . From  $\omega_e$  we may obtain a stretching force constant of  $k_e = 2.10 \pm 0.01\text{ mdyn/\AA}$ . This may be compared with the dimer force constant of  $2.44\text{ mdyn/\AA}$ . If we assume the stretch along the coordinate of the totally symmetric mode ( $\nu_1$ ) to be governed by a Morse potential we may calculate a spectroscopic atomization energy ( $\text{Rh}_3 \rightarrow 3\text{Rh}$ ) to be  $D_e^{\text{at}} = \omega_e^2/4\omega_e x_e = 6.6 \pm 1.4\text{ eV}$ .

Despite the fact that, due to our optically thin samples we observed no absorption (SDS) spectra, we are able to obtain a sensitive Raman excitation profile by plotting the observed intensity of individual Raman lines against excitation wavelength. We display several in Fig. 2. A broadband ranging over 540–590 nm with maximum around 575 nm is observed for the  $n\nu_1$  vibrations. For weaker lines, less distinct profiles are obtained. For the line at  $247.9\text{ cm}^{-1}$  in the range 576–584 nm, a slow rise to  $\sim 582\text{ nm}$  is observed

TABLE I. Resonance Raman lines observed for rhodium trimers in argon matrices. Excitation wavelength is the range of laser excitation wavelengths over which each line is observed.

$\lambda_{\text{ex}}$ (nm)	Raman lines ( $\text{cm}^{-1}$ )	Assignment
540–590	247.9(8)	$\nu_3(a_1)$
579–583	259	$\nu_2(b_1)$
540–590	321.9(5)	$\nu_1(a_1)$
576–582	400	$A$ state
581–583	496	$2\nu_3$
579–583	545	$2\nu_2$
540–590	641.9(11)	$2\nu_1$
540–590	961.6(17)	$3\nu_1$
540–590	1279.4(20)	$4\nu_1$
540–590	1597.4(14)	$5\nu_1$

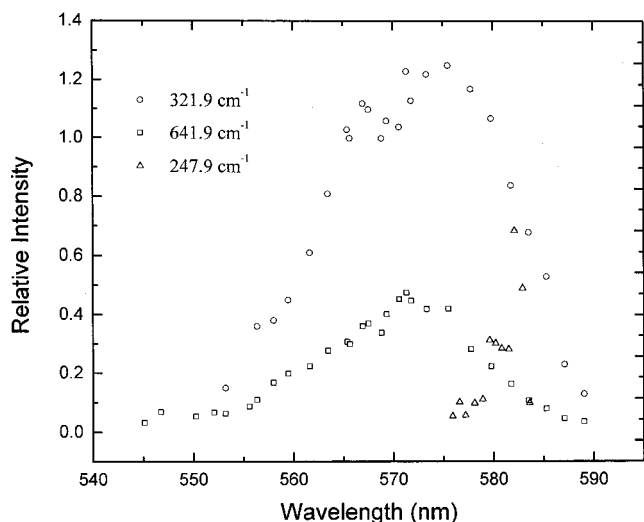


FIG. 2. The Raman excitation profile for the frequency of  $322.1\text{ cm}^{-1}(\nu_1)$ ,  $642.7\text{ cm}^{-1}(2\nu_1)$ , and  $247.9\text{ cm}^{-1}(\nu_3)$ .

followed by an abrupt decline. Other lines show profiles which are too noisy to plot.

#### IV. DISCUSSION

There have been several previous studies of rhodium trimers. Ozin and Hanlan<sup>3</sup> examined the optical absorption spectrum of various rhodium clusters as well as their behavior under photolysis. Van Zee, Hamrich, and Weltner<sup>4</sup> examined dimers and trimers of Co, Rh, and Ir using ESR, while Balasubramanian and co-workers applied the technique of complete active space multiconfiguration self-interaction (CASSCF) plus multireference configuration-interaction (MRSDCI) calculations to both low spin<sup>6</sup> and high spin<sup>5</sup> states of rhodium trimers. Chien *et al.*<sup>7</sup> have carried out density functional calculations on small Rh clusters.

Using argon-metal vapor deposition techniques, varying the relative concentration of metal/argon, Ozin and Hanlan<sup>3</sup> examined the absorption spectroscopy of rhodium clusters in the visible and UV region. As the metal/argon ratios are increased, new bands are observed which they assign to successively larger clusters. They identified bands at 400 nm and 460 nm which they assigned to  $\text{Rh}_2$ , one at 490 nm assigned to  $\text{Rh}_3$ , and a band around 560 nm assigned to higher clusters  $\text{Rh}_n$ . In our earlier work on the rhodium dimer, using the excitation profile, we showed that the band at 490 nm definitely corresponds to the dimer. In this work, we observe no Raman excitation of the trimer in the region of 490 nm, but that a band peaking at 575 nm is clearly associated with the trimer. These reassignments illustrate the advantage of using Raman excitation profiles combined with mass-selection to definitively identify optical transitions in metal clusters.

Van Zee *et al.*<sup>4</sup> examined the ESR spectrum of rhodium trimer and found that the ground state was of high spin, most likely  $S=5/2$ , and observed a hyperfine intensity pattern of 1:3:3:1, which indicates  $D_{3h}$  equilateral triangle geometry. Dai and Balasubramanian,<sup>5</sup> however, in a calculation involving high-spin low-lying state of the  $\text{Rh}_3$  predict a  ${}^6A_1$  ground

state with an apical angle of  $50.8^\circ$  for the ground state. This state is derived along with a nearby  ${}^6B_2$  (0.02–0.08 eV) state via Jahn-Teller distortion of an  ${}^6E'(D_{3h})$  state. The calculations of Chien, Blaisten-Barojas, and Pederson<sup>7</sup> predict a value of  $\omega_e=322\text{ cm}^{-1}$  for an equilateral triangle geometry using the local density approximation. This is in remarkable agreement with our experiment. They also confirm the  ${}^6A_1$  nature of the ground state indicating a slight distortion from  $D_{3h}$  symmetry, in agreement with the SCF calculation of Balasubramanian. Our observations of three distinct fundamentals confirm the  $C_{2v}$  geometry for the ground state, although using a simple central force field<sup>11</sup> calculation, we obtain an apical angle of  $76.9^\circ$ . It is also possible that matrix interactions have caused an otherwise equilateral  $D_{3h}$  geometry to distort lifting the double vibrational degeneracy. Either way, these observations are not inconsistent with the ESR experiments if the barrier to pseudorotation is sufficiently small that the ESR may be considered to be obtained as an average over all configurations.

Additional confirmation of this is provided by our observation of a low lying (A) state at  $400\text{ cm}^{-1}$  (0.05 eV). Note, although we cannot develop a clear excitation profile for this state, it is observed only in the relatively narrow region 582–576 nm, almost exactly the same region as the  $\nu_2(b_1)$  vibration of the ground (X) state. It is commonly assumed that resonance Raman spectra can only involve totally symmetric ground state species. This is only true if the symmetry of both ground and excited state involved in the optical resonance are the same or in the absence of strong vibronic mixing. Observation of the  $\nu_2(b_1)$  vibration indicates that least for the subregion 582–576 nm the usual resonance Raman selection rule breaks down allowing transitions to states which are nontotally symmetric. Due to the similarity in excitation profile and the observed energy, it is quite likely that the (A) state at  $400\text{ cm}^{-1}$  is the  ${}^6B_2$  state predicted by Balasubramanian.

It remains to discuss our determination of the energy of atomization. In their earlier paper on low spin states of  $\text{Rh}_3$ , Das and Balasubramanian<sup>6</sup> predicted a value of 8.15 eV, but in their later high spin calculation,<sup>5</sup> revise this to 10.8 eV. They do point out that using the trimer dissociation energy ( $\text{Rh}_3\rightarrow\text{Rh}_2+\text{Rh}$ ) obtained in photolytic experiments of Ozin and Hanlan<sup>3</sup> (4.16 eV) plus the dissociation energy for the dimer ( $D_e=2.92\text{ eV}$ ) (Ref. 2) gives an experimental value of 7.08 eV. This is in agreement with our spectroscopic value of  $6.6\pm 1.4\text{ eV}$ , but both values deviate considerably from the revised value calculated by Balasubramanian. They are actually close to his original value. The density functional calculations of Chien *et al.*<sup>7</sup> all predict atomization energies close to our result.

#### ACKNOWLEDGMENTS

The authors are grateful to Professor K. Balasubramanian for helpful discussions and clarification. This work was supported by the National Science Foundation under Cooperative Agreement No. RII-9353488 and Grant No. CHE-9712031 and by the City University of New York PSC-BHE Faculty Research Award Program.

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