

The bond energy of Rh₂

Jon D. Langenberg and Michael D. Morse

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

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In a spectroscopic investigation of jet-cooled Rh₂ by the resonant two-photon ionization method, an abrupt predissociation threshold is observed in a dense set of vibronic levels at $19\,405 \pm 4\text{ cm}^{-1}$. Based on the high density of states expected in the rhodium dimer, the sharp definition of the predissociation threshold that is observed, and the validation of a similar conclusion in the case of V₂, it is argued that predissociation occurs as soon as the energy of the separated ground state atoms is exceeded. On this basis the bond energy of Rh₂ is assigned as $D_0(\text{Rh}_2) = 19\,405 \pm 4\text{ cm}^{-1} = 2.4059 \pm 0.0005\text{ eV}$. This value is compared to the results of other experiments and to theoretical calculations. The bond energy of disilver, $D_0(\text{Ag}_2) = 1.65 \pm 0.03\text{ eV}$, provides a particularly useful standard of comparison, and suggests that 4*d* contributions to the bond energy of Rh₂ amount to at least 0.76 eV. © 1998 American Institute of Physics. [S0021-9606(98)01606-7]

I. INTRODUCTION

The open *d* subshells of the transition metals often lead to considerable electronic complexity in diatomic molecules containing a single transition metal atom;¹ when two open *d* subshell transition metal atoms are bonded to one another the number of low-lying electronic states can become so vast that a classification of vibronic levels into electronic states becomes impossible. In these molecules it is not uncommon to reach densities of states such that vibronic levels of the same symmetry are spaced less than 10 cm^{-1} apart. Under these conditions spin-orbit and nonadiabatic interactions can lead to such strongly mixed levels that it becomes fundamentally incorrect to think of the molecule as moving on a single potential energy curve. When this occurs below the energy of ground state separated atoms, predissociation sets in abruptly as soon as the dissociation energy is exceeded. In more than 20 examples this effect has been exploited to measure the bond energy to spectroscopic precision.²⁻¹² In this article we present the results of such a measurement for the dirhodium molecule, Rh₂.

Despite advances in theoretical methodology and computational facilities, transition metal molecules remain difficult systems for the chemical theorist. Electron correlation and exchange effects are critical for the proper description of the chemical bond, and relativistic effects including spin-orbit interaction must be carefully evaluated if the calculation is to provide a meaningful result. Furthermore, the balance among these effects may be quite delicate; therefore, they must be calculated to a similar degree of accuracy if a reasonable model for the electronic structure of the molecule is to be obtained. The bond energy is among the most difficult properties to calculate correctly; as such, it provides a particularly sensitive test of the accuracy of a calculation.

The dirhodium molecule, Rh₂, has been the subject of several theoretical studies, but no consensus has emerged regarding the nature of the ground state or the properties of the molecule. Only on the spin multiplicity (quintet, $S=2$) is there agreement. The broad disagreement among these stud-

ies stands as testimony to the difficulties encountered in theoretical work on the transition metal dimers. Table I provides a summary of theoretical¹³⁻²⁰ and experimental^{21,22} results relevant to the Rh₂ ground state which have appeared in the literature to date. In addition to these results Ozin and Hanlan have identified several electronic absorptions of matrix isolated Rh₂ between 208 and 460 nm.²³ Some of these had been previously observed by Brom *et al.*, who considered them to be transitions in atomic rhodium.²⁴

The first of the calculations reported in Table I is a SCF- $X\alpha$ -SW calculation performed in 1978.¹³ We now know that this method is unreliable, particularly for the transition metal dimers; it should therefore be disregarded. The same is true for the CASSCF-CI calculation reported in Ref. 14. This entry in Table I is taken from a compendium of calculations on the 3*d* and 4*d* dimers that is now known to predict bond lengths that are far too large and bond energies that are far too small. These results are generally incorrect except for dimers such as Ni₂ in which no significant *d*-orbital contributions to the bond exist.²

The next study of Rh₂, reported by Balasubramanian and Liao in 1989,¹⁵ probably is the most accurate of the variationally-based calculations. This conclusion is based on the fact that electron correlation is typically more accurately treated in the separated atoms than in the molecule, so that the energy calculated for the separated atoms is nearly always closer to the true value than that calculated for the molecule. Since the variational principle guarantees that the calculated energies lie above the true energies, this implies that the dissociation energy will be underestimated with most variational methods. Exceptions are methods based on coupled-pair theories and many-body perturbation theory, which are size-consistent.²⁵ On this basis the calculation of Balasubramanian and Liao¹⁵ is probably the most accurate of the variational calculations, and the bond energy of Rh₂ is probably greater than 2.1 eV. It is common for variational calculations which suffer from insufficient electron correlation to both underestimate the bond energy and overestimate the bond length. Based on a comparison to the work of Bala-

TABLE I. Calculated and measured properties of the Rh₂ ground state.

Ground state	Leading configuration	Bond length (Å)	ω_e (cm ⁻¹)	D_e (eV)	Method	Reference (year)
NP ^a	NP ^a	2.39	NP ^a	NP ^a	SCF- $X\alpha$ -SW	13 (1978)
⁵ Σ_g^+	$9\sigma_g^2 10\sigma_g^2 5\pi_u^3 2\delta_g^3 2\delta_u^3 5\pi_g^3 9\sigma_u^2$	2.86	118	0.85	CASSCF/CI	14 (1985)
⁵ Δ_g	$9\sigma_g^2 10\sigma_g^2 5\pi_u^4 2\delta_g^4 2\delta_u^3 5\pi_g^3 9\sigma_u^1$	2.28	266	2.1	CASSCF/MRCI	15 (1989)
⁵ $\Delta_g(4_g)$		2.26	305	NP ^a	CASSCF/CI/RCI	15 (1989)
⁵ Δ_u	$9\sigma_g^2 10\sigma_g^2 5\pi_u^4 2\delta_g^3 2\delta_u^4 5\pi_g^2 9\sigma_u^1$	2.673	238	1.50	Pseudopotential MRCI	16 (1990)
NP ^a	NP ^a	2.39	NP ^a	2.59	DFT "low spin"	17 (1990)
NP ^a	NP ^a	2.49	NP ^a	1.96	DFT "high spin"	17 (1990)
NP ^a	NP ^a	2.291	331	NP ^a	Pseudopotential DFT	18 (1993)
NP ^a	NP ^a	2.268	301	NP ^a	All electron DFT	18 (1993)
⁵ Σ_u	NP ^a	2.22–2.36	NP ^a	NP ^a	DFT	19 (1994)
$S=2$	NP ^a	2.589	204	1.33	Effective core potential DFT	20 (1996)
			$\omega_e = 283.9 \pm 1.8$	1.4 ± 0.3^b	Resonance Raman in solid argon	21 (1997)
			$\omega_{e,x_e} = 1.83 \pm 0.33$			
				2.92 ± 0.22	Knudsen effusion	22 (1974)
				2.4059 ± 0.0005	This work	

^aNot provided in the reference cited.

^bEstimated from the relationship $D_e = \omega_e^2 / (4\omega_{e,x_e})$, which is valid for a Morse potential.

subramanian and Liao,¹⁵ it appears that the more recent calculation by Illas *et al.*¹⁶ suffers from this problem.

The more recent density functional theory studies^{17–20} of Rh₂ are not bound by the variational principle, and can either overestimate or underestimate the bond energy. It is rare, however, for recent implementations of this method to seriously underestimate the bond length. On this basis, the density functional calculation of Chen *et al.*¹⁸ probably provides the best estimate of the ground state properties of Rh₂ from this theoretical starting point; unfortunately, no electronic configuration, term symbol, or bond energy is provided in this calculation. The all-electron calculation, however, predicts essentially the same values of the bond length and vibrational frequency as reported by Balasubramanian and Liao. This agreement lends credence to both studies.

In addition to these theoretical investigations, two previous experimental studies are relevant to this work. In 1974 Cocke and Gingerich measured the gas phase chemical equilibria,



and



among others, in the temperature range of 2461–2536 K.²² The temperature range was insufficient to determine bond energies by the second law method; the third law method was used to derive a value of the Rh₂ bond energy of 2.92 ± 0.22 eV.²² This value exceeds all of the theoretical estimates of the Rh₂ bond energy as well as the value we report below. Possible causes of this discrepancy are discussed in Sec. IV.

A final experiment on Rh₂ was reported in early 1997 by Wang *et al.*²¹ A mass selected beam of Rh₂⁺, sputtered from a cooled rhodium target, was slowed to ~ 10 eV, neutralized, and deposited in an argon matrix at ~ 14 K. A weak absorp-

tion feature at 495 nm was detected by scattering depletion spectroscopy, and irradiation with argon ion laser lines between 457.9 nm and 514.5 nm permitted the $\nu = 1-4$ vibrational levels of the ground state to be measured by resonance Raman spectroscopy. From this work values of $\omega_e = 283.9 \pm 1.8$ cm⁻¹ and $\omega_{e,x_e} = 1.83 \pm 0.33$ cm⁻¹ were derived. Assuming that the potential is well-described by a Morse potential all the way to dissociation, the well-known relationship²⁶

$$D_e = \omega_e^2 / (4\omega_{e,x_e}) \quad (1.4)$$

provides $D_e = 1.4 \pm 0.3$ eV for Rh₂.²¹ This value is substantially smaller than that reported in the more reliable theoretical calculations as well as the Knudsen effusion result.²² It is also much smaller than the value deduced in the present study. Reasons for the discrepancies between these experimental values are considered below. The implications of our measured value for the bonding in Rh₂ are discussed as well.

II. EXPERIMENT

A jet-cooled beam of rhodium clusters was generated by pulsed laser ablation (532 nm, 5 mJ/pulse, focused to ~ 300 μm) of a rhodium metal target disk, which was rotated and translated to prevent drilling a hole through the material. The ablated metal atoms and ions were entrained in a pulsed expansion of helium (~ 120 psig, 99.998% purity), which was timed to place a high pressure of helium over the target when the ablation laser was fired. After supersonic expansion and passage through a skimmer (~ 1 cm diam), the rhodium clusters that were generated entered the ionization region of a reflectron time-of-flight mass spectrometer employing the Wiley–McLaren extraction scheme.²⁷ Here the molecules were probed by radiation generated either by a Nd:YAG-pumped dye laser or a Nd:YAG-pumped optical parametric oscillator/amplifier system (Continuum Mirage 500, pumped by a seeded Continuum Powerlite 8000 Nd:YAG laser). Dirhodium molecules that were successfully

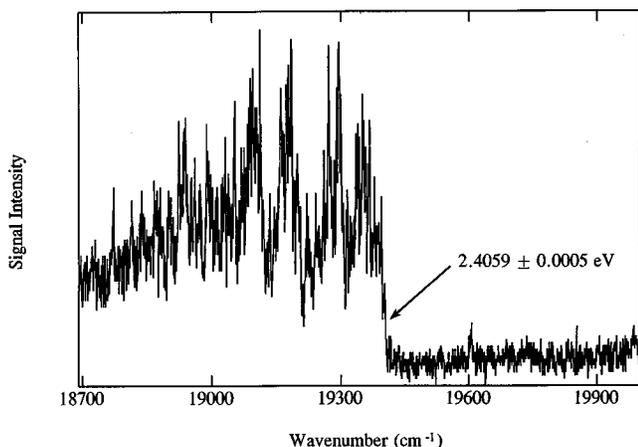


FIG. 1. A resonant two-photon ionization scan of $^{103}\text{Rh}_2$ over the range from 18 700 to 20 000 cm^{-1} reveals a sharp predissociation threshold at $19\,405 \pm 4 \text{ cm}^{-1}$. This is assigned as the bond energy of Rh_2 .

excited were then ionized using 193 nm radiation produced by an excimer laser operating on an argon fluoride mixture. The resulting ions were separated by mass and detected using a microchannel plate detector. The output of the detector was preamplified, digitized, and processed in a 386-based PC clone, which controlled the entire experiment. The tunable radiation used to record the spectrum was calibrated by conducting a pressure-tuned high resolution scan (0.03 cm^{-1}) while simultaneously recording the fluorescence spectrum of I_2 . This was compared to the absorption atlas of Gerstenkorn and Luc²⁸ to provide an accurate absolute calibration of the recorded spectra.

III. RESULTS

Figure 1 displays the spectrum of $^{103}\text{Rh}_2$ over the range from 18 700 to 19 900 cm^{-1} . The most notable features in the spectrum are the spectral congestion in the red portion of this range and the abrupt drop in signal at $19\,405 \pm 4 \text{ cm}^{-1}$. To the blue of this wave number only background noise is observed. The main source of uncertainty in the measurement of the threshold comes from difficulties in determining where the signal first rises above the background noise. The quoted error limit represents our best estimate of the uncertainty in locating the threshold.

As mentioned in the Introduction, similar predissociation thresholds have now been measured in over 20 transition metal molecules,²⁻¹² and it has been argued that in cases in which a sharp threshold is observed and the density of expected electronic states is large, the predissociation threshold occurs precisely at the lowest dissociation limit.⁶ Of course, this presupposes that the ground states of the separated atoms can combine to generate potential curves with the same values of the good quantum numbers Ω , g/u , and for $\Omega = 0$, $+/-$ as are found for the molecular states which are produced by electric dipole excitations from the ground molecular state.^{5,11}

The assertion that predissociation occurs as soon as the energy of the ground state separated atoms is exceeded has been convincingly demonstrated by four independent measurements on atomic vanadium, V_2 , and V_2^+ . It is well-

known that the dissociation energies $D_0(\text{M}_2)$ and $D_0(\text{M}_2^+)$ are related to the ionization energies $\text{IE}(\text{M})$ and $\text{IE}(\text{M}_2)$ by the thermochemical cycle

$$D_0(\text{M}_2) + \text{IE}(\text{M}) - D_0(\text{M}_2^+) - \text{IE}(\text{M}_2) = 0. \quad (3.1)$$

In the case of vanadium all four quantities are independently known, so that Eq. (3.1) may be used to test our assertion that predissociation sets in as soon as it is energetically possible. From an extended series of measurements on the Rydberg levels of atomic vanadium, James and co-workers have established that $\text{IE}(\text{V}) = 54\,411.67 \pm 0.17 \text{ cm}^{-1}$.¹⁰ From pulsed-field ionization, zero electron kinetic energy measurements on V_2 , Yang and co-workers have established that $\text{IE}(\text{V}_2) = 51\,271.1 \pm 0.5 \text{ cm}^{-1}$.²⁸ From measurements of the predissociation threshold of V_2 , $D_0(\text{V}_2) = 22\,201 \pm 1 \text{ cm}^{-1}$.⁵ Finally, measurements of the predissociation threshold of V_2^+ provide $D_0(\text{V}_2^+) = 25\,326 \pm 15 \text{ cm}^{-1}$.⁸ The relatively large uncertainty associated with this last value is due to a somewhat gradual rise in atomic V^+ fragment signal as the threshold is crossed. This probably results from difficulty in cooling the rotational degrees of freedom in V_2^+ under the conditions of the experiment, since conditions leading to effective rotational cooling also lead to charge neutralization and loss of the V_2^+ signal. In any event, these four independently measured values may be combined to give $D_0(\text{V}_2) + \text{IE}(\text{V}) - D_0(\text{V}_2^+) - \text{IE}(\text{V}_2) = 15.6 \pm 15 \text{ cm}^{-1}$, where the uncertainty in the result is entirely due to the uncertainty in measuring $D_0(\text{V}_2^+)$. The agreement between this result and the required value of zero demonstrates convincingly that V_2 and V_2^+ do predissociate as soon as the energy of the separated atoms is exceeded, and strongly suggests that similar behavior will occur in other transition metal dimers having a large density of states at the energy of ground state separated atoms. In addition, by expressing $D_0(\text{V}_2^+)$ in terms of the more accurately known quantities it becomes possible to refine the value to give $D_0(\text{V}_2^+) = 25\,341.6 \pm 1.2 \text{ cm}^{-1}$. The lower value previously reported,⁸ $25\,326 \pm 15 \text{ cm}^{-1}$, is consistent with the hypothesis of poor rotational cooling in V_2^+ .

It is difficult to accurately estimate the density of electronic states in diatomic molecules such as V_2 and Rh_2 , but some feeling for this can be obtained by counting the number of distinct Hund's case (c) potential curves arising within an energy, E , of the ground separated atom limit. The resulting integrated density of states, $N(E)$, has values of 383, 1883, and 2711 at energies of 1000, 5000, and 10000 cm^{-1} , respectively, in the case of V_2 .²⁹ It is this incredible density of electronic states that causes predissociation to set in precisely at the lowest separated atom limit. For Rh_2 smaller values of $N(E)$ of 55, 463, and 1295 are obtained at $E = 1000, 5000,$ and 10000 cm^{-1} , respectively.²⁹ Although these values of $N(E)$ are smaller than those found for V_2 , they are still quite large and probably sufficient to cause extensive nonadiabatic mixing near the ground state separated atom limit. On this basis we assign the measured predissociation threshold as the bond energy of Rh_2 , giving $D_0(\text{Rh}_2) = 19\,405 \pm 4 \text{ cm}^{-1}$, or $2.4059 \pm 0.0005 \text{ eV}$.

IV. DISCUSSION

The Rh₂ bond energy obtained in this study, 2.406 eV, is significantly smaller than that obtained in the previous Knudsen effusion study, 2.92±0.22 eV.²² The Knudsen effusion value was based on a third law determination, however, and this method can present problems because of the difficulty in estimating the absolute entropy of the diatomic transition metal. To determine whether this was the source of the problem we recalculated the Rh₂ bond energy using the *ab initio* results of Balasubramanian and Liao to estimate the absolute entropy of Rh₂ at the high temperature of the experiment. To our surprise, this led to almost no change in the Knudsen effusion value of $D_0(\text{Rh}_2)$. Other potential problems, mentioned in the Knudsen effusion study, include progressive enlargement of the effusion orifice at the high temperatures employed and the existence of platinum impurities in the rhodium sample. Enlargement of the effusion orifice leads to a greater flow rate, shifting the process from pure effusion toward a mild supersonic expansion. Any clustering occurring during the expansion could then lead to formation of Rh₂ molecules, artificially increasing their apparent concentration and causing $D_0(\text{Rh}_2)$ to be overestimated. Likewise, reaction of atomic platinum with carbon in the graphite-lined cell produces PtC, one isotope of which falls at the same mass as Rh₂. Again, this would artificially increase the apparent concentration of Rh₂, causing $D_0(\text{Rh}_2)$ to be overestimated. Although the investigators attempted to correct for both of these problems, they remain likely causes for the discrepancy with the present study.

The other experimental datum relevant to $D_0(\text{Rh}_2)$ comes from the resonance Raman experiments of Wang *et al.*²¹ In their study accurate values of ω_e and $\omega_e x_e$ were obtained from Rh₂ isolated in an argon matrix. Straightforward application of the Morse potential formula, $D_e = \omega_e^2 / (4\omega_e x_e)$, then provided $D_e = 1.4 \pm 0.3$ eV. The uncertainty in this result, ±0.3 eV, was obtained simply by propagation of the uncertainties in ω_e and $\omega_e x_e$, and did not take into account any possible departures from the Morse potential form. As Wang *et al.* point out,²¹ however, departures from the Morse potential form are possible in the transition metal dimers because *d-d* bonding optimizes at shorter distances than *s-s* bonding. The resonance Raman experiments only probed levels up to an energy of 1097 cm⁻¹, so it is certainly possible that significant deviations from the Morse potential form could occur as one moves to higher energy, particularly since the region probed represents only 6%–10% of the well depth.

A likely explanation of the discrepancy between the Morse potential result, $D_e = 1.4 \pm 0.3$ eV, and the predissociation threshold measurement, $D_0 = 2.406$ eV, is that as one stretches the Rh₂ bond the *d-d* bonds break before the *s-s* bond. Only at short internuclear distances can the *4d* orbitals overlap and bond, forming the deep, narrow part of the potential curve around the potential minimum. The more diffuse *5s* orbitals overlap and bond at larger internuclear distances, and are expected to exhibit a broader range of distances over which they interact. The net result could be a deep, narrow inner well followed by a shelf or even a second

minimum at larger internuclear distances. Using vibrational parameters based only on the region around the potential minimum to derive a value of D_e may ignore the contribution of the *5s*σ_g orbital to the bond, thereby underestimating the bond energy.

A clear-cut example of this sort of problem is provided by Cr₂, which has been carefully studied by mass-selected negative ion photodetachment spectroscopy.³⁰ The first nine vibrational levels of the ground state are well-described by $\omega_e = 480.6$ cm⁻¹ and $\omega_e x_e = 14.1$ cm⁻¹. Application of the Morse potential formula then predicts $D_e = 4095$ cm⁻¹ or 0.508 eV. This seriously underestimates the true bond energy of Cr₂, which has been determined to be 1.44±0.05 eV by Knudsen effusion mass spectrometry.³¹ This result is also verified by guided ion beam mass spectrometry, which provides $D_0(\text{Cr}_2) = 1.42 \pm 0.10$ eV.³² The existence of a deep, narrow well at small internuclear distances, followed by a broad shelflike structure at larger separations is supported by detailed analysis of the photoelectron data³⁰ and by theoretical calculations on Cr₂.³³ Much more work is required to demonstrate unequivocally that a similarly shaped ground state potential curve exists for Rh₂.

The existence of *d* orbital contributions to the bonding in Rh₂ may be demonstrated and, to a degree, even quantified by comparison to the bond energy of Ag₂. In Ag the *4d* orbitals are greatly contracted relative to the *5s* orbital, making them rather inaccessible for chemical bonding. In addition, the *4d* orbitals are completely filled in the Ag and Ag₂ ground states, leading to a cancellation of *4d* bonding and antibonding effects in Ag₂. Thus the bond in Ag₂ is essentially due only to *5s* orbital interactions, making Ag₂ an excellent standard of comparison to evaluate the *4d* contributions to the bonding in the late *4d* series of transition metal dimers.

The bond energy of Ag₂ has been measured by Knudsen effusion mass spectrometry on several occasions, and all are in good agreement, giving $D_0(\text{Ag}_2) = 1.65 \pm 0.03$ eV.^{34,35} This is substantially reduced from the bond energies of its congeners Cu₂ and Au₂, 2.061±0.025 (Ref. 36) and 2.306±0.005 eV,³⁷ respectively, because of the larger size of the *5s* orbital in silver ($\langle r \rangle = 1.826$ Å) (Ref. 38) as compared to the *4s* ($\langle r \rangle = 1.726$ Å) (Ref. 38) and *6s* ($\langle r \rangle = 1.620$ Å) (Ref. 38) orbitals of copper and gold. The even larger size of the *5s* orbital in the *4d*⁸*5s*¹, ⁴*F* ground state of rhodium ($\langle r \rangle = 1.909$ Å) (Ref. 38) suggests that the *5s* contributions to the Rh₂ bond will be even smaller than 1.65 eV. Since no atomic promotion is required to prepare the ground state Rh atoms to form a *5s*σ_g² bond, it is straightforward to estimate the *4d* contribution to the bond energy of Rh₂ as at least 2.41 – (1.65±0.03) eV = 0.76±0.03 eV.

V. CONCLUSION

The bond energy of Rh₂ has been measured by the abrupt onset of predissociation in a congested vibronic spectrum of the jet-cooled molecule. The resulting value, $D_0(\text{Rh}_2) = 19\,405 \pm 4$ cm⁻¹ = 2.4059±0.0005 eV, is significantly less than that obtained in a previous Knudsen effusion study, yet substantially greater than previous theoretical in-

vestigations. On the basis of comparisons to the filled d -subshell homologue, Ag_2 , it is argued that $4d$ orbital interactions in Rh_2 contribute at least 0.76 eV to the bond energy.

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