

Mass-analyzed threshold ionization of an excited state of lanthanum dioxide

Lu Wu, Yang Liu, Changhua Zhang, Shenggang Li, David A. Dixon et al.

Citation: *J. Chem. Phys.* **137**, 034307 (2012); doi: 10.1063/1.4734312

View online: <http://dx.doi.org/10.1063/1.4734312>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v137/i3>

Published by the [American Institute of Physics](#).

Additional information on J. Chem. Phys.

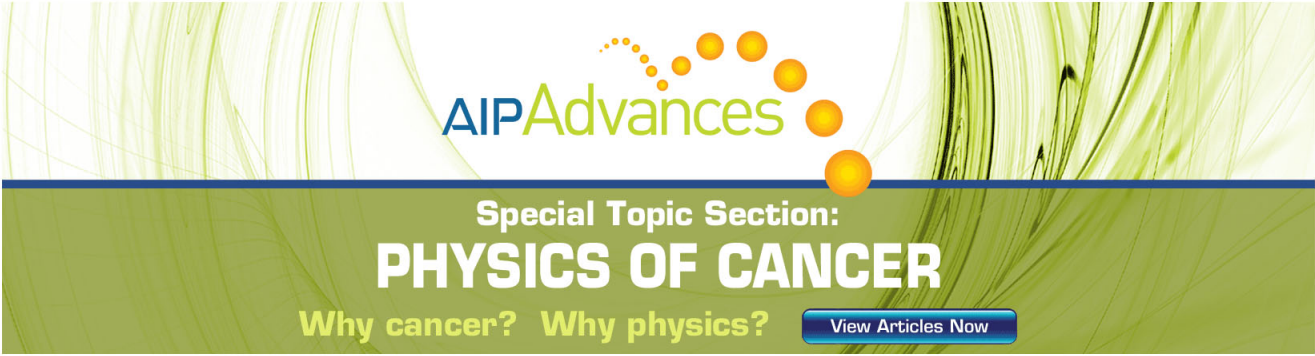
Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



AIPAdvances

Special Topic Section:
PHYSICS OF CANCER

Why cancer? Why physics? [View Articles Now](#)

Mass-analyzed threshold ionization of an excited state of lanthanum dioxide

Lu Wu,¹ Yang Liu,^{1,a)} Changhua Zhang,^{1,b)} Shenggang Li,^{2,c)} David A. Dixon,² and Dong-Sheng Yang^{1,d)}

¹Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055, USA

²Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487-0336, USA

(Received 21 May 2012; accepted 23 June 2012; published online 17 July 2012)

LaO₂ was produced in a pulsed laser-vaporization molecular beam source and studied by mass-analyzed threshold ionization (MATI) spectroscopy and *ab initio* electronic structure calculations. The calculations included density functional theory, second-order perturbation theory, coupled cluster theory, and complete active space self-consistent field methods. The adiabatic ionization energy of the molecule and vibrational frequencies of the molecule and its cation were measured accurately for the first time from the MATI spectrum. Numerous ionization processes of lanthanum dioxide, peroxide, and superoxide were considered; the ³B₂ ← ⁴B₂ electronic transition of the dioxide was assigned upon comparison with the observed spectrum. The ionization energy and O-La-O bending frequency of the ⁴B₂ neutral state are 4.9760 (6) eV and 92 cm⁻¹, respectively. The La-O stretching and O-La-O bending frequencies of the ³B₂ cationic state are 656 and 122 cm⁻¹, respectively. The ⁴B₂ state is formed by two electron transfer from lanthanum to oxygen atoms, and the ³B₂ state is produced by the further removal of a lanthanum 6s-based electron. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4734312>]

I. INTRODUCTION

Transition metal oxides are widely used as both catalysts and catalyst supports in chemical processes. The widespread and important applications of transition metal oxides have motivated numerous research groups to study their physical and chemical properties in the gas phase, where complicating factors such as solvents and counterions are removed. For transition metal oxide cations, extensive studies have been reported on their reactivity,^{1–4} UV-Vis photofragmentation,^{5–7} and infrared (IR) multiphoton photodissociation or single-photon vibrational predissociation.^{8–16} The studies of the anions were largely carried out with photoelectron spectroscopy,^{17–32} and additional investigations were reported about their reactivity^{1,3,33–36} and IR photodissociation.^{12,37–39} Neutral metal oxides are more challenging to study experimentally because they are difficult to size-select, and their formation and properties are usually determined by ionization techniques, including multiphoton IR (Ref. 40) and single-photon UV (Refs. 41–43) and vacuum UV laser ionization.^{44–47} In addition, neutral metal oxides have also been studied by matrix-isolation IR spectroscopy.⁴⁸ In spite of the extensive studies, the current knowledge about the electronic states and molecular structures of polyatomic tran-

sition metal oxide clusters is largely derived from theoretical predictions. However, the reliable prediction of the electronic and geometric structures is often complicated by the presence of many low energy structural isomers and a high density of low-lying electronic states of each isomer. Thus, inconsistent theoretical results have often been reported on the nature of the ground electronic states and minimum energy structures of both polyatomic neutral molecules^{49,50} and ions.^{12,51,52} Therefore, a reliable identification of the molecular structures and electronic states for transition metal oxide clusters and their ions generally requires confirmation by spectroscopic measurements, especially by high resolution spectroscopic techniques.

Although diatomic transition metal oxides have been well studied, the spectroscopy of their polyatomic metal oxides is rather limited.^{53,54} As one of the simplest polyatomic transition metal oxides, LaO₂ has been studied previously by gas-phase guided ion beam mass spectrometry,⁵⁵ chemielectron spectroscopy,^{56–59} and argon matrix-isolation IR spectroscopy.⁶⁰ Clemmer *et al.*⁵⁵ investigated the thermochemistry of LaO₂ and LaO₂⁺ formed in endothermic reactions between LaO⁺ and NO₂ in a guided ion beam mass spectrometer. In that study, the bond dissociation energies D₀(OLa-O) and D₀⁺(OLa⁺-O) were measured as 4.20(33) and 0.99(31) eV, respectively, and the ionization energy (IE) of LaO₂ was 8.11(35) eV. Cockett *et al.*^{56–58} reported chemielectron spectra obtained for the reactions of La atom with O₂ in the X³Σ_g⁻ and a¹Δ_g electronic states and assigned spectra to chemiionization of lanthanum dioxide formed by association reactions. In the spectrum of La + O₂ (X³Σ_g⁻), they observed two partially resolved vibrational progressions separated by 250 (50) cm⁻¹ with an averaged interval of

^{a)}Present address: Academy of Fundamental and Interdisciplinary Science, Harbin Institute of Technology, Harbin 150080, People's Republic of China.

^{b)}Present address: Institute of Atomic and Molecular Physics, Sichuan University, Chengdu, Sichuan 610065, People's Republic of China.

^{c)}Present address: Low Carbon Energy Conversion Technology Center, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201203, People's Republic of China.

^{d)}Electronic mail: dyang0@uky.edu.

660 (30) cm^{-1} . They assigned the 250 cm^{-1} separation to the symmetric O-La-O bending mode and the 660 cm^{-1} interval to the symmetric La-O stretching mode of the LaO_2^+ cation. Andrews *et al.* obtained IR spectra for the reactions of laser-ablated La, La^+ and electrons with O_2 in argon matrix and observed La-O symmetric stretching frequencies of 570 cm^{-1} for LaO_2 and 689 cm^{-1} for the LaO_2^- anion.⁶⁰ It is interesting to note that the stretching frequency of the LaO_2^+ cation measured from the gas-phase chemielectron spectrum is similar to that of the LaO_2^- , but is substantially different from that of the LaO_2 molecule from the argon matrix-isolation IR spectra. More recently, Todorova *et al.* reexamined the chemiionization reactions of $\text{La} + \text{O}_2$ using *ab initio* electronic structure calculations.⁶¹ In that study, a bent C_{2v} structure was predicted for the neutral lanthanum dioxide in the $^2\text{B}_1$ ground state and a linear structure for the cation in the $^1\Sigma_g^+$ ground state. The ionization and bond dissociation energies of LaO_2 were calculated to be 7.99–8.70 and 6.47–6.71 eV, respectively, depending on the level of theory. A requirement for a chemiionization reaction of a metal oxide molecule to take place is that its dissociation energy must be greater than its ionization energy. Because the dissociation energy was smaller than the IE, it was concluded that the chemiionization reaction $\text{La} + \text{O}_2 \rightarrow \text{LaO}_2^+ + e^-$ was endothermic and should not have contributed to the chemielectron spectra. As an alternative, a two-step process was proposed for the formation of the chemielectrons under the $\text{La} + \text{O}_2$ ($X^3\Sigma_g^-$) reactions conditions, which included $\text{La} + \text{O}_2 \rightarrow \text{LaO} + \text{O}$ and $\text{La} + \text{O} \rightarrow \text{LaO}^+ + e^-$. However, because the measured vibrational interval (660 cm^{-1}) in the chemielectron spectrum is too small for the La-O stretching frequency of the diatomic LaO^+ ion (>800 cm^{-1}),^{60,61} LaO may not be the carrier of the chemielectrons.

A third hypothesis may be that the chemielectrons were produced by ionization of an excited electronic state of LaO_2 . However, nothing is known about any excited states of the molecule. The objective of this work is to search for and characterize the excited states of LaO_2 . The LaO_2 molecule is produced in a pulsed laser-vaporization molecule beam source and characterized by mass-analyzed threshold ionization (MATI) spectroscopy and electronic structure calculations.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

A. Experimental

The metal-cluster beam MATI spectrometer used in this work is similar to the ZEKE apparatus described in a previous publication.⁶² It consists of two vacuum chambers. The first houses a Smalley-type cluster source and is pumped by a 2200 l s^{-1} diffusion pump. The second chamber houses a time-of-flight spectrometer and is pumped by two 400 l s^{-1} turbo molecular pumps. The time-of-flight spectrometer is composed of a two stage extraction assembly, a 34 cm long flight tube, and a dual microchannel plate detector (Burle). The entire spectrometer is housed in a cylindrical, double-walled μ -metal shield.

Lanthanum oxides were produced by laser vaporization (Lumonics YM-800 Nd:YAG, 532 nm) of a La rod (Alfa Aesa, 99.9%) in the presence of a pulse of ultra-high-purity He (or Ar) carrier gas delivered by a homemade piezoelectric pulsed valve.⁶³ The metal vapor and carrier gas passed down a clustering tube (2 mm inner diameter, 2 cm length), and the resultant clusters were supersonically expanded into the vacuum chamber. The supersonic jet was skimmed (2 mm diameter) 3 cm downstream from the exit end of the clustering tube. A pair of deflection plates (2.5 cm spacing, 220V) located after the skimmer was used to remove residual charged species (formed during laser ablation) from the molecular beam before it entered the second chamber.

Prior to the MATI measurements, photoionization time-of-flight mass spectra were recorded to determine the chemical content of the cluster beam, and pulsed-field-ionization photoionization efficiency spectra were recorded to locate the ionization threshold of LaO_2 . With the ionization laser set above the ionization threshold, the experimental conditions (e.g., timing and power of the vaporization and ionization lasers and the backing pressure of the carrier gas) were carefully optimized to maximize the intensity of the LaO_2^+ signal in the mass spectrum.

With the optimized experimental conditions, LaO_2 was excited to high-lying Rydberg states in a single-photon process by the frequency-doubled output of a dye laser (Lumonics HD-500) pumped by a Nd:YAG laser (Quanta Ray GCR-3, 355 nm) and then ionized by an electric pulse (DEI PVM-4140, 320 V cm^{-1}). The laser beam was collinear and counter propagating with the molecule beam. The time delay between the laser and electric pulses was varied to maximize the MATI signal, and it was typically 20 μs for He carrier and 50 μs for Ar. A small dc field (4.1 V cm^{-1}) was applied to help separate the prompt ions produced by direct photoionization from the MATI ions produced by delayed field ionization. The MATI signal was obtained by scanning the wavelength of the tunable dye laser, detected by a dual microchannel plate detector, amplified by a preamplifier (SRS SR445), averaged by a gated integrator (SRS SR250), and stored in a laboratory computer. Laser wavelengths were calibrated against vanadium atomic transitions in the spectral region.⁶⁴ The Stark shift induced by the dc field was calculated using the relation of $\Delta E = 6.1E_f^{1/2}$, where E_f is in V cm^{-1} and ΔE in cm^{-1} .⁶⁵

B. Computational

Density functional theory (DFT) and *ab initio* molecular orbital theory methods were used to calculate equilibrium geometries and vibrational frequencies of the low-lying electronic states of LaO_2 and LaO_2^+ . Single-reference calculations included DFT with Becke's three parameter hybrid functional with the correlation functional of Lee, Yang, and Parr (B3LYP),^{66,67} second-order Møller-Plesset (MP2) perturbation,⁶⁸ and coupled cluster with single, double and perturbative triple excitations (CCSD(T))^{69,70} methods. The oxygen atomic orbitals were described by the augmented correlation-consistent triple zeta (aug-cc-pVTZ) basis set⁷¹ or the 6-311g(d) valence triple split basis set.⁷² La atomic

orbitals were represented by the Stuttgart-type relativistic effective core potential basis with 28 core electrons, that is, Stuttgart RSC ANO/ECP.⁷³ All of these single-reference calculations were carried out with GAUSSIAN 09 program.⁷⁴

Multi-reference methods, complete active space self-consistent field (CASSCF)^{75,76} and CAS with second-order perturbation theory (CASPT2),⁷⁷ were used to characterize electron configurations of the electronic states of lanthanum dioxide and its cation. A level shift technique⁷⁸ was employed, if necessary, to avoid intruder state problems in the CASPT2 calculations. In the CASSCF and CASPT2 calculations, the full-electron atomic natural orbital with relativistic core correlation (ANO-RCC)⁷⁹ basis set and the second-order Douglas–Kroll–Hess Hamiltonian^{80,81} were employed to treat the scalar relativistic effect. In the ANO-RCC basis, the primitive set of (24s,21p,15d,5f,3g,2h) was contracted to (11s,10p,8d,5f,3g,2h) for the La atom, and the (14s, 9p, 4d, 3f, 2g) primitive set was contracted to (8s, 7p, 4d, 3f, 2g) for the O atom. Because the La atom has an outmost valence electron configuration of $5d^1 6s^2$, three electrons and six orbitals (6s and 5d) were included in the complete active space for the La atom. Because the O atom has a valence electron configuration of $2p^4$, four electrons and three orbitals (2p) were used in the active space for each O atom. Thus, the active space for the LaO_2 molecule included 11 electrons and 12 orbitals, i.e., (11, 12), and that for LaO_2^+ was (10, 12). All of the multi-reference calculations were performed using MOLPRO 2010.1 program.⁸²

To compare with the experimental spectrum, Franck-Condon (FC) factors were calculated using the equilibrium geometries, harmonic frequencies, and normal mode coordinates of the neutral molecule and cation.^{83–85} In these calculations, recursion relations⁸⁶ were employed and the Duschinsky effect⁸⁷ was taken into consideration. Spectral simulation was obtained using the experimental linewidth and a Lorentzian line shape. Transitions from excited vibrational levels of the neutral molecule were considered by assuming thermal excitation at specific temperatures.

III. RESULTS AND DISCUSSION

A. MATI spectrum

Figure 1(a) presents the MATI spectrum of LaO_2 seeded in He carrier gas. LaO_2 was formed without addition of external oxygen gas. The presence of oxygen was due to either the impurity of the He gas or to the La rod. The spectrum displays the most intense band at 40134 (5) cm^{-1} or 4.9760 (6) eV and a major progression of the 656 (1) cm^{-1} . Nested inside the major progression is a second progression with intervals of 122 (1) cm^{-1} . In addition, the spectrum exhibits a weak band 92 (1) cm^{-1} below each member of the 656 cm^{-1} progression. The energy of the origin band corresponds to the adiabatic IE of a neutral state of the molecule. The 656 and 122 cm^{-1} progressions are due to transitions from the ground vibrational level of a neutral state to vibrational levels of two modes of an ion state, whereas the 92 cm^{-1} weak bands are due to transitions from an excited vibrational level of a neutral mode to the ion. At first view, the 122 cm^{-1} progression

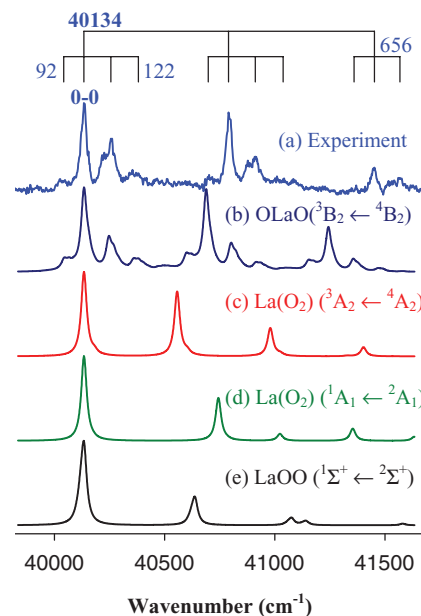


FIG. 1. MATI spectrum of LaO_2 seeded in He (a) and simulations (100 K) of the ${}^3B_2 \leftarrow {}^4B_2$ transition of lanthanum dioxide (OLaO) (b), the ${}^3A_2 \leftarrow {}^4A_2$ (c) and ${}^1A_1 \leftarrow {}^2A_1$ (d) transitions of lanthanum peroxide ($\text{La}(\text{O}_2)$), and the ${}^1\Sigma^+ \leftarrow {}^2\Sigma^+$ transition of lanthanum superoxide (LaOO) (e).

was thought to be vibrational sequence bands from excited vibrational levels of a neutral mode to various levels of an ion mode. However, additional measurements with Ar or He/Ar carriers show no changes of the relative intensity (though the signal was weaker), indicating they are not vibrational hot bands.⁸⁸ Moreover, if these transitions were sequence bands, the frequency difference between the neutral and ionic modes would be as large as 122 cm^{-1} . Such a large frequency difference suggests a large geometry change from the neutral molecule to the ion, inconsistent with the observed short FC profile.

The LaO_2 molecule and its cation may be linear or bent. A linear structure could have a $D_{\infty h}$ symmetry (OLaO) with one totally symmetric vibrational mode (σ_g^+) or a $C_{\infty v}$ symmetry (LaOO) with two symmetric modes (σ^+), whereas a bent structure could have a C_{2v} symmetry (OLaO) with two symmetric modes (a_1) or a C_s symmetry (LaOO) with three symmetric modes (a'). Because the spectrum displays two active vibrational modes of 656 and 122 cm^{-1} for the ion state, LaO_2^+ should be in a bent C_{2v} (or C_s) structure or a linear $C_{\infty v}$ geometry from the viewpoint of the first-order selection rule. Because the spectrum exhibits a strong origin band and a short FC intensity profile, both the neutral and ion states should be in the same structural configuration, as a linear-bent conversion between the two states would produce a spectrum with a very weak origin band and a long FC intensity profile. As discussed in the Introduction, Todorova *et al.* reported a theoretical study of the gas-phase chemiionization reactions of La with oxygen atoms or molecules.⁶¹ Using DFT and *ab initio* molecular orbital theory methods, they predicted the ground states of LaO_2 and LaO_2^+ to be 2B_1 (C_{2v}) and ${}^1\Sigma_g^+$ ($D_{\infty h}$), respectively, and the IE values for the ionization process of $\text{LaO}_2^+ ({}^1\Sigma_g^+, D_{\infty h}) \leftarrow \text{LaO}_2 ({}^2B_1, C_{2v})$ to be in the range of 7.99 – 8.70 eV. Obviously, this

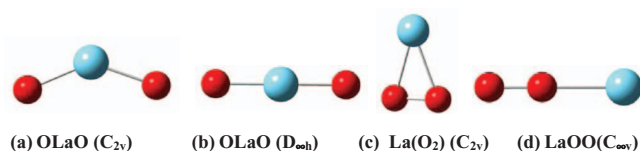


FIG. 2. Possible structures of LaO_2 : lanthanum dioxide (OLaO) (a, b), lanthanum peroxide [$La(O_2)$] (c), and lanthanum superoxide (LaOO) (d). A bent lanthanum superoxide was also considered, but it converged to the linear structure upon geometry optimization.

ionization process cannot be associated with the observed spectrum, as the predicted IEs are more than 3.0 eV higher than the measured value and the bent-linear structural conversion would yield a much longer FC profile than the experimental spectrum. To help assign the electronic states and molecular structures involved in the MATI transitions, we performed an extensive theoretical search of molecular structures and electronic states, and the results are described below.

B. Low-lying electronic states of lanthanum dioxide (OLaO), lanthanum peroxide ($La(O_2)$), lanthanum superoxide (LaOO), and their cations

Figure 2 shows the possible structures of LaO_2 that were considered in our calculations. These structures include bent and linear lanthanum dioxides (OLaO), bent lanthanum peroxide ($La(O_2)$), and linear lanthanum superoxide (LaOO). A bent lanthanum superoxide was also considered, but it was converged to the linear structure upon geometry optimization. Table I summarizes the electronic states and energies, geome-

tries, and vibrational frequencies from the DFT/B3LYP calculations. Among all the oxides, the OLaO dioxide is the most stable isomer, followed by the $La(O_2)$ peroxide and the LaOO superoxide. For the OLaO dioxide, the bent structure (C_{2v}) is slightly more stable than the linear structure. The ground electronic state of the bent dioxide is predicted to be 2B_2 . Above the 2B_2 state, a 4B_2 state is located at 3.40 eV. Ionization of the 2B_2 state of the bent oxide yields a linear structure ($D_{\infty h}$) in the ${}^1\Sigma_g^+$ ionic state; on the other hand, ionization of the 4B_2 state leads to a 3B_2 ionic state also in the bent configuration. The ${}^1\Sigma_g^+$ ionic state could also be formed from ionization of the ${}^2\Sigma_u^+$ neutral state, which is 0.05 eV above the 2B_2 state. The prediction of the 2B_2 and ${}^1\Sigma_g^+$ states are consistent with the previous calculations.⁶¹ However, the 4B_2 and ${}^2\Sigma_u^+$ neutral states and the 3B_2 ionic state are reported for the first time. (It is noted that the 2B_2 state was previously labeled as 2B_1 because of a different axis orientation in the Cartesian coordinate system.)

For the $La(O_2)$ peroxide (C_{2v}), the ground state of the neutral molecule is 2A_1 , followed by an excited 4A_2 state at ~ 2.3 eV; the ground state of the cation is 1A_1 , followed by an excited 3A_1 state at ~ 2.2 eV. The structural differences between the dioxide and peroxide are very clear. For example, the $\angle O-La-O$ angle and the O-O distance in the 2B_2 state of the dioxide are 146.3° and 3.73 Å, whereas the corresponding angle and distance in the 2A_1 state of the peroxide are 42.0° and 1.49 Å, respectively. The O-O distance in the dioxide is too far apart to have any significant interaction between the oxygen atoms, while the O-O distance in the peroxide is close to the characteristic length of a single O-O bond (1.48 Å).⁸⁹ Moreover, the O-O stretching frequency of the $La(O_2)$ 2A_1 state

TABLE I. Electronic states, geometries (R for La-O of OLaO and La-O/O-O of LaOO and $La(O_2)$, A for $\angle O-La-O$ or $\angle La-O-O$), vibrational frequencies (ν_1),^a relative energies (E_{rel}), and adiabatic ionization energies (AIE) of lanthanum dioxide (OLaO, C_{2v} or $D_{\infty h}$), lanthanum peroxide [$La(O_2)$, C_{2v}], and lanthanum superoxide (LaOO, $C_{\infty v}$) from the B3LYP calculations with aug-cc-pvtz basis set for O atoms and SDD ECP basis set for the La atom.

States	R (Å)	A ($^\circ$)	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	E_{rel} (eV)	AIE (eV)
OLaO							
2B_2 (C_{2v})	1.95	146.3	622	142	388	0	9.03 (${}^3B_2 \leftarrow {}^2B_2$)
${}^2\Sigma_u^+$ ($D_{\infty h}$)	1.95	180.0	609	56	457	0.05	8.68 (${}^1\Sigma_g^+ \leftarrow {}^2B_2$)
4B_2 (C_{2v})	2.17	118.9	494	90	445	3.40	8.63 (${}^1\Sigma_g^+ \leftarrow {}^2\Sigma_u^+$) 5.63 (${}^3B_2 \leftarrow {}^4B_2$)
(OLaO) ⁺							
${}^1\Sigma_g^+$ ($D_{\infty h}$)	1.83	180.0	631	194	750	8.68	
3B_2 (C_{2v})	2.10	114.7	555	113	487	9.03	
$La(O_2)$							
2A_1 (C_{2v})	2.08/1.49	42.0	872	573	481	2.01	7.72 (${}^3A_2 \leftarrow {}^2A_1$)
4A_2 (C_{2v})	2.36/1.33	32.6	1203	382	335	4.34	5.56 (${}^1A_1 \leftarrow {}^2A_1$) 5.39 (${}^3A_2 \leftarrow {}^4A_2$)
[$La(O_2)$] ⁺							
1A_1 (C_{2v})	2.03/1.49	43.0	890	610	521	7.57	
3A_2 (C_{2v})	2.29/1.32	33.6	1197	423	383	9.73	
LaOO							
${}^2\Sigma^+$ ($C_{\infty v}$)	1.93/1.37	180.0	942	504	188	3.98	6.04 (${}^1\Sigma^+ \leftarrow {}^2\Sigma^+$)
(LaOO) ⁺							
${}^1\Sigma^+$ ($C_{\infty v}$)	1.92/1.33	180.0	990	525	203	10.02	

^aFor C_{2v} or $D_{\infty h}$ dioxide, ν_1 , ν_2 , and ν_3 are the symmetric La-O stretch (a_1 or σ_g^+), O-La-O bend (a_1 or π_u), and antisymmetric La-O stretch (b_2 or σ_u^+), respectively. For C_{2v} peroxide, ν_1 , ν_2 , and ν_3 are the symmetric O-O stretch (a_1), symmetric La-O₂ stretch (a_1), and antisymmetric La-O₂ stretch (b_2), respectively. For $C_{\infty v}$ superoxide, ν_1 , ν_2 , and ν_3 are symmetric O-O stretch (σ^+), symmetric La-O stretch (σ^+), and degenerate La-O-O bend (π), respectively.

is predicted to be 872 cm^{-1} , which is very close to the O-O stretching frequencies of 878 or 866 cm^{-1} of hydrogen peroxide (H_2O_2).⁹⁰ For the LaOO superoxide ($\text{C}_{\infty\text{v}}$), the ground states of the neutral molecule and cation are predicted to be $^2\Sigma^+$ and $^1\Sigma^+$, respectively. The O-O distance ($1.37\text{ \AA}$) in the $^2\Sigma^+$ neutral state is comparable to the bond length of molecular oxygen anion (O_2^-) ($1.35\text{ \AA}$)⁹¹ and to the characteristic bond length of a superoxide compound ($1.34\text{ \AA}$).⁸⁹ The O-O bond in the LaOO can be considered to have a bond order of 1.5 and an averaged bond distance of the double and single O-O bonds. The calculated O-O stretching frequency (942 cm^{-1}) in the $^2\Sigma_g^+$ neutral state of LaOO is also close to that of hydrogen superoxide radical ($\text{HOO}\cdot$) (929 cm^{-1})⁹⁰ and comparable to that of molecular oxygen anion (1090 cm^{-1}).⁹¹

C. Ionization of an excited state of lanthanum dioxide (OLaO)

The electronic transition responsible for the observed MATI spectrum can be determined by comparing the measured and predicted AIEs, vibrational frequencies, and intensity profiles. As discussed in Sec. II A, the experimental AIE is 4.9760 eV , and the measured frequencies are 656 and 122 cm^{-1} for the cation and 92 cm^{-1} for the neutral molecule. From Table I, the AIEs of the $^3\text{B}_2 \leftarrow ^2\text{B}_2$, $^1\Sigma_g^+ \leftarrow ^2\text{B}_2$, and $^1\Sigma_g^+ \leftarrow ^2\Sigma_u^+$ transitions of the OLaO dioxide are predicted to be 9.03 , 8.68 , and 8.63 eV , respectively, and the AIE of the $^3\text{A}_2 \leftarrow ^2\text{A}_1$ ionization of the $\text{La}(\text{O}_2)$ peroxide is 7.72 eV . Because the predicted AIEs are 3.0 eV higher than the measured AIE and the difference is much larger than any expected computational errors, the above transitions can safely be excluded from the MATI spectrum. On the other hand, the predicted AIEs of the $^3\text{B}_2 \leftarrow ^4\text{B}_2$ transition of the dioxide, the $^1\text{A}_1 \leftarrow ^2\text{A}_1$ and $^3\text{A}_2 \leftarrow ^4\text{A}_2$ transitions of the peroxide, and the $^1\Sigma^+ \leftarrow ^2\Sigma^+$ transition of the superoxide are all much closer to the experimental value.

For these cases, the comparison of the experimental and theoretical AIEs alone is not sufficient for the electronic-state assignment. Therefore, vibrational frequencies are considered as well. Table I shows that none of the vibrational frequencies of the $^1\Sigma^+$ state of $(\text{LaOO})^+$ and the $^3\text{A}_2$ state of $[\text{La}(\text{O}_2)]^+$ matches the measured 656 or 122 cm^{-1} vibrational intervals. Although the symmetric bending frequency (ν_2) of the $[\text{La}(\text{O}_2)]^+ ^1\text{A}_1$ state (610 cm^{-1}) is in reasonable agreement with the 656 cm^{-1} interval, the singlet ionic state does not show any frequency comparable to the 122 cm^{-1} mode. In addition, none of the initial states in the $^1\text{A}_1 \leftarrow ^2\text{A}_1$ and $^3\text{A}_2 \leftarrow ^4\text{A}_2$ transitions of the peroxide and the $^1\Sigma^+ \leftarrow ^2\Sigma^+$ transition of the superoxide exhibits a mode comparable to the measured 92 cm^{-1} mode. Thus, none of the above three transitions should be associated with the MATI spectrum. On the other hand, the symmetric O-La-O bending frequencies (ν_2) of the $^4\text{B}_2$ and $^3\text{B}_2$ states of the OLaO dioxide (90 and 113 cm^{-1}) are in excellent agreement with the observed vibrational intervals of 92 and 122 cm^{-1} , even though the calculated symmetric La-O stretching frequency (ν_1 , 555 cm^{-1}) of the $^3\text{B}_2$ state at the B3LYP level is substantially

underestimated when compared to the experimental value of 656 cm^{-1} . Considering both the AIE and the vibrational frequencies, $^3\text{B}_2 \leftarrow ^4\text{B}_2$ is the most likely transition probed by the MATI experiment. This conclusion is further supported by considering the spectral intensity profile. Figures 1(b)–1(e) show the simulations from transitions of $^3\text{B}_2 \leftarrow ^4\text{B}_2$ of OLaO, $^3\text{A}_2 \leftarrow ^4\text{A}_2$ and $^1\text{A}_1 \leftarrow ^2\text{A}_1$ of $\text{La}(\text{O}_2)$, and $^1\Sigma^+ \leftarrow ^2\Sigma^+$ of LaOO. In these simulations, the calculated frequencies are not scaled, but the theoretical AIEs are shifted to the experimental origin band for comparison. Frequency scaling is often used for the high-frequency modes of organic molecules, but from our previous studies of numerous metal complexes, the scaling practice does not work for the low-frequency vibrational modes.⁹² Low-frequency metal-ligand vibrational modes are more difficult to treat theoretically, and predicted values can be on either side of the experimental measurements. As shown in Figure 1, the $^3\text{A}_2 \leftarrow ^4\text{A}_2$ and $^1\text{A}_1 \leftarrow ^2\text{A}_1$ transitions of $\text{La}(\text{O}_2)$ (Figures 1(c) and 1(d)) and the $^1\Sigma^+ \leftarrow ^2\Sigma^+$ transition of LaOO (Figure 1(e)) fail to reproduce the experimental 122 cm^{-1} progression and the 92 cm^{-1} hot bands. On the other hand, the simulation of the $^3\text{B}_2 \leftarrow ^4\text{B}_2$ transition of OLaO (Figure 1(b)) is in very good agreement with the experimental spectrum.

In an attempt to improve the theoretical AIEs and vibrational frequencies, calculations at higher levels of theory were carried out for the observed $^3\text{B}_2$ and $^4\text{B}_2$ states of OLaO. Table II summarizes the spectroscopic constants from MATI measurements and DFT/B3LYP, MP2, CCSD, CCSD(T) and CASPT2 calculations. The wave-function-based *ab initio* methods yield slightly better AIEs (5.37 – 5.39 eV) than the DFT method (5.55 eV). For the vibrational analysis of the $^3\text{B}_2$ ionic state, the MP2 method produces the best frequency for the La-O stretching mode (ν_1 , 601 cm^{-1}), whereas the CASPT2 method gives the best frequency for the O-La-O bending mode (ν_2 , 121 cm^{-1}). For the O-La-O bending mode (ν_2) of the $^4\text{B}_2$ neutral state, the B3LYP, MP2, CCSD, CASPT2 and CCSD(T) calculations all give bending frequencies within less than 15 cm^{-1} of experiment, the accuracy expected for such a low frequency mode. No single method produces uniform results matching the experimental values. The biggest issue is that all of the methods underestimate the value of the stretching frequency for the $^3\text{B}_2$ ionic state by 50 to 100 cm^{-1} .

Figure 3(a) presents the valence electron configuration of the $^4\text{B}_2$ state of OLaO, $1a_1^2 1b_2^2 1a_2^2 1b_1^2 2a_1^1 2b_2^1 3a_1^1$, from the CASPT2 calculations. $1a_1^2 1b_2^2 1a_2^2 1b_1^2 2a_1^1 2b_2^1$ are oxygen 2p-based orbitals and $3a_1^1$ (highest occupied molecular orbital, HOMO) is a La 6s-based orbital. Because the ground electron configuration of La is $5d^1 6s^2$, the formation of the $^4\text{B}_2$ state of OLaO results in two-electron transfer from the metal to oxygen atoms. Thus, the formal oxidation states of O and La in the $^4\text{B}_2$ state are -1.0 and $+2.0$, respectively. Ionization of the $^4\text{B}_2$ neutral state removes the La 6s-based electron from the HOMO and gives a $^3\text{B}_2$ ion ground state. Because the HOMO is essentially a non-bonding orbital, the ion state has a similar geometry to the neutral state and the MATI spectrum has a short FC intensity profile. In contrast to the $^4\text{B}_2$ state, the $^2\text{B}_2$ state has an electron configuration of $1b_2^2 1a_2^2 1a_1^2 1b_1^2 2a_1^2 2b_2^1$, where the HOMO ($2b_2^1$) is an

TABLE II. Electronic states, geometries ($R_{\text{La-O}}$ and $A_{\angle\text{O-La-O}}$), and vibrational frequencies (ν_i)^a of the $^4\text{B}_2$ and $^3\text{B}_2$ states and adiabatic ionization energies (AIE) of the $^4\text{B}_2$ state of bent lanthanum dioxide (OLaO, C_{2v}) from MATI spectroscopy and theoretical calculations.^b

Method		$R_{\text{La-O}}$ (Å)	$A_{\angle\text{O-La-O}}$ (°)	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	AIE(eV)
MATI	$^4\text{B}_2$				92		4.9760(6)
	$^3\text{B}_2$			656	122		
CASPT2 ^c	$^4\text{B}_2$	2.18	118.8	490	105	497	5.57
	$^3\text{B}_2$	2.12	113.5	556	121	551	
B3LYP	$^4\text{B}_2$	2.17	119.1	512	86	449	5.55
	$^3\text{B}_2$	2.10	114.7	562	107	487	
MP2	$^4\text{B}_2$	2.16	117.5	548	86	543	5.53
	$^3\text{B}_2$	2.10	112.2	601	98	605	
CCSD	$^4\text{B}_2$	2.17	118.8	535	89	526	5.38
	$^3\text{B}_2$	2.11	114.0	586	94	583	
CCSD(T)	$^4\text{B}_2$	2.16	119.5	530	82	510	5.37
	$^3\text{B}_2$	2.10	112.0	565	65	563	

^aThe vibrational modes of ν_1 , ν_2 , and ν_3 are the symmetric La-O stretch (a_1), O-La-O bend (a_1), and antisymmetric La-O stretch (b_2), respectively.

^bThe ANO-RCC basis set on La and O was used for the CASPT2 calculations. The Stuttgart RSC ANO/ECP basis set on La and 6-311G(d) basis set on O were used for the other calculations.

^cVibrational frequencies calculated at the CASSCF levels.

oxygen 2p-base orbital (Figure 3(b)). The formation of the $^2\text{B}_2$ state leads to three electron loss of La to O. Thus, the formal oxidation states of La and O in this case are -1.5 and $+3.0$, respectively. Because the HOMO is an oxygen 2p-based orbital, the removal of this electron requires much higher energy in the presence of the $+3$ lanthanum field. This explains why the predicted AIE of the $^2\text{B}_2$ state is much higher than that of the $^4\text{B}_2$ state.

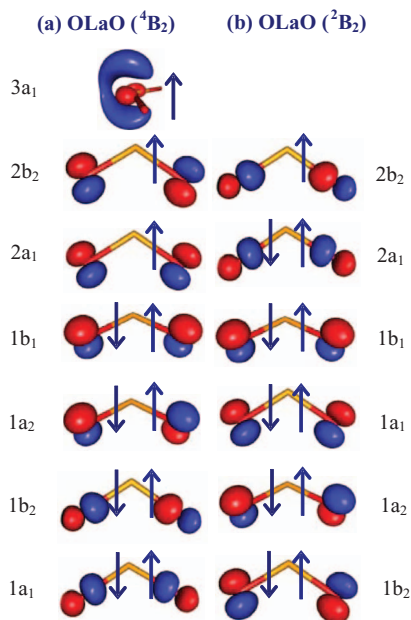


FIG. 3. Valence electron configurations of the $^4\text{B}_2$ (a) and $^2\text{B}_2$ (b) states of lanthanum dioxide (OLaO). The molecule is placed on the yz plane. The relative energy orderings of the valence molecular orbitals are different in the two states. Two electrons are transferred from La to two O atoms in the formation of the $^4\text{B}_2$ state, which has the HOMO of largely a La 6s character. On the other hand, three electrons are transferred from La to two O atoms to form the $^2\text{B}_2$ state, which has the HOMO of largely an O 2p character.

Dissociation of the $^4\text{B}_2$ excited state of OLaO could give the La atom in an excited state ^4F and the O_2 molecule in an excited state of $a^1\Delta_g$ with spin conservation. The ^4F ($5d^26s^1$) state is 0.33 eV above the ground state $^2\text{D}(5d^16s^2)$.^{64,93} The dissociation energies of this process are predicted to be 5.81 , 5.38 , and 5.25 eV by the B3LYP, MP2, and CCSD(T) calculations. The dissociation energy is slightly larger than the AIE at the B3LYP level, but slightly smaller at the MP2 and CCSD(T) levels (Table II). Due to the inconsistent trends of the predicted dissociation and ionization energies, no conclusion could be made about whether the previous chemielectron spectrum^{56–58} was produced by ionization of the OLaO $^4\text{B}_2$ state. However, because the La-O stretching frequency of the $[\text{OLaO}]^+ ^3\text{B}_2$ state (656 (1) cm^{-1}) measured from our MATI spectrum is consistent with the value (660 (30) cm^{-1}) from the chemielectron spectrum, LaO_2 seems to be the carrier of the chemielectrons. An accurate measurement for the dissociation energy of the OLaO $^4\text{B}_2$ state is required to settle this problem in a more definitive manner.

IV. CONCLUSIONS

A MATI spectrum is reported for the first time for LaO_2 seeded in a supersonic molecular beam. The spectrum exhibits a strong origin band, La^+-O stretching and $\text{O-La}^+-\text{O}$ bending progressions, and thermal excitation of the O-La-O bending mode. Our combined experimental and computational analysis shows that the spectrum involves ionization of an excited high spin electronic state of lanthanum dioxide. This process is determined to be the $^3\text{B}_2 \leftarrow ^4\text{B}_2$ transition. The $^4\text{B}_2$ excited neutral state is formed by transferring two La electrons to oxygen atoms and has a valence electron configuration consisting of oxygen 2p- and lanthanum 6s-based orbitals. The $^3\text{B}_2$ state is formed by the removal of the non-bonding La 6s electron and has a molecular geometry similar to the $^4\text{B}_2$ neutral state. The ground state of the lanthanum dioxide was predicted to be a doublet, but it was not observed

by the experiment, most likely because of its much higher ionization energy. In addition to possible transitions of the dioxide, ionization processes of lanthanum peroxide and superoxide were considered as well, but they were excluded after comparison with the experimental spectrum. This is the first example where a single-photon MATI spectrum is observed from an excited initial electronic state lying several electronvolts above the ground electronic state.

ACKNOWLEDGMENTS

We are grateful for the financial support from the National Science Foundation Division of Chemistry (Chemical Structure, Dynamics and Mechanisms, CHE-1012351). We also acknowledge additional support from the donors of the Petroleum Research Fund of the American Chemical Society and the Kentucky Science and Engineering Foundation. This work was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, U.S. Department of Energy (DOE) under Grant No. DE-FG02-03ER15481 (catalysis center program). D.A.D. also thanks the Robert Ramsay Chair Fund of The University of Alabama for support.

- ¹D. K. Bohme and H. Schwarz, *Angew. Chem. Int. Ed.* **44**, 2336 (2005).
- ²D. R. Justes, N. A. Moore, and A. W. Castleman, Jr., *J. Phys. Chem. B* **108**, 3855 (2004).
- ³K. A. Zemski, D. R. Justes, and A. W. Castleman, Jr., *J. Phys. Chem. B* **106**, 6136 (2002).
- ⁴K. A. Zemski, R. C. Bell, and A. W. Castleman, Jr., *J. Phys. Chem. A* **104**, 5732 (2000).
- ⁵K. S. Molek, C. Anfuso-Cleary, and M. A. Duncan, *J. Phys. Chem. A* **112**, 9238 (2008).
- ⁶K. S. Molek, T. D. Jaeger, and M. A. Duncan, *J. Chem. Phys.* **123**, 144313/1 (2005).
- ⁷Z. D. Reed and M. A. Duncan, *J. Phys. Chem. A* **112**, 5354 (2008).
- ⁸A. Fielicke, C. Ratsch, G. von Helden, and G. Meijer, *J. Chem. Phys.* **127**, 234306 (2008).
- ⁹K. R. Asmis, M. Bruemmer, C. Kaposta, G. Santambrogio, G. von Helden, G. Meijer, K. Rademann, and L. Woeste, *Phys. Chem. Chem. Phys.* **4**, 1101 (2002).
- ¹⁰K. R. Asmis, A. Fielicke, G. von Helden, and G. Meijer, *Chem. Phys. Solid Surf.* **12**, 327 (2007).
- ¹¹K. R. Asmis, G. Meijer, M. Bruemmer, C. Kaposta, G. Santambrogio, L. Woeste, and J. Sauer, *J. Chem. Phys.* **120**, 6461 (2004).
- ¹²K. R. Asmis and J. Sauer, *Mass Spectrom. Rev.* **26**, 542 (2007).
- ¹³K. Demyk, D. van Heijnsbergen, G. von Helden, and G. Meijer, *Astron. Astrophys.* **420**, 547 (2004).
- ¹⁴A. Fielicke, G. Meijer, and G. von Helden, *Eur. Phys. J. D* **24**, 69 (2003).
- ¹⁵A. Fielicke, G. Meijer, and G. von Helden, *J. Am. Chem. Soc.* **125**, 3659 (2003).
- ¹⁶G. von Helden, A. Kirilyuk, D. van Heijnsbergen, B. Sartakov, M. A. Duncan, and G. Meijer, *Chem. Phys.* **262**, 31 (2000).
- ¹⁷S. M. E. Green, S. Alex, N. L. Fleischer, E. L. Millam, T. P. Marcy, and D. G. Leopold, *J. Chem. Phys.* **114**, 2653 (2001).
- ¹⁸L.-S. Wang, *Adv. Ser. Phys. Chem.* **10B**, 854 (2000).
- ¹⁹X. Yang, T. Waters, X.-B. Wang, R. A. J. O'Hair, A. G. Wedd, J. Li, D. A. Dixon, and L.-S. Wang, *J. Phys. Chem. A* **108**, 10089 (2004).
- ²⁰H.-J. Zhai, J. Doeblner, J. Sauer, and L.-S. Wang, *J. Am. Chem. Soc.* **129**, 13270 (2007).
- ²¹H.-J. Zhai, X. Huang, T. Waters, X.-B. Wang, R. A. J. O'Hair, A. G. Wedd, and L.-S. Wang, *J. Phys. Chem. A* **109**, 10512 (2005).
- ²²N. O. Jones, S. N. Khanna, T. Baruah, M. R. Pederson, W. J. Zheng, J. M. Nilles, and K. H. Bowen, *Phys. Rev. B: Condens. Matter Mater. Phys.* **70**, 134422/1 (2004).
- ²³S. N. Khanna, P. Jena, W. J. Zheng, J. M. Nilles, and K. H. Bowen, *Phys. Rev. B: Condens. Matter Mater. Phys.* **69**, 144418/1 (2004).
- ²⁴R. B. Wyrwas, B. L. Yoder, J. T. Maze, and C. C. Jarrold, *J. Phys. Chem. A* **110**, 2157 (2006).
- ²⁵B. L. Yoder, J. T. Maze, K. Raghavachari, and C. C. Jarrold, *J. Chem. Phys.* **122**, 094313 (2005).
- ²⁶A. Pramann, K. Koyasu, A. Nakajima, and K. Kaya, *J. Phys. Chem. A* **106**, 4891 (2002).
- ²⁷A. Pramann, K. Koyasu, A. Nakajima, and K. Kaya, *J. Chem. Phys.* **116**, 6521 (2002).
- ²⁸A. Pramann, Y. Nakamura, A. Nakajima, and K. Kaya, *J. Phys. Chem. A* **105**, 7534 (2001).
- ²⁹Y. D. Kim and G. Gantefor, *Chem. Phys. Lett.* **383**, 80 (2004).
- ³⁰Q. Sun, P. Jena, Y. D. Kim, M. Fischer, and G. Gantefor, *J. Chem. Phys.* **120**, 6510 (2004).
- ³¹Q. Sun, B. K. Rao, P. Jena, D. Stolcic, G. Gantefor, and Y. Kawazoe, *Chem. Phys. Lett.* **387**, 29 (2004).
- ³²Q. Sun, B. K. Rao, P. Jena, D. Stolcic, Y. D. Kim, G. Gantefor, and A. W. Castleman, Jr., *J. Chem. Phys.* **121**, 9417 (2004).
- ³³R. G. Keese, B. Chen, A. C. Harms, and A. W. Castleman, Jr., *Int. J. Mass Spectrom. Ion Process.* **123**, 225 (1993).
- ³⁴W. D. Vann, R. L. Wagner, and A. W. Castleman, *J. Phys. Chem. A* **102**, 1708 (1998).
- ³⁵W. D. Vann and A. W. Castleman, Jr., *J. Phys. Chem. A* **103**, 847 (1999).
- ³⁶S. W. Sigsworth and A. W. Castleman, Jr., *J. Am. Chem. Soc.* **114**, 10471 (1992).
- ³⁷K. R. Asmis, G. Santambrogio, M. Bruemmer, and J. Sauer, *Angew. Chem., Int. Ed.* **44**, 3122 (2005).
- ³⁸S. Feyel, H. Schwarz, D. Schroder, C. Daniel, H. Hartl, J. Dobler, J. Sauer, G. Santambrogio, L. Woste, and K. R. Asmis, *Chem. Phys. Chem.* **8**, 1640 (2007).
- ³⁹G. Santambrogio, M. Bruemmer, L. Woeste, J. Doeblner, M. Sierka, J. Sauer, G. Meijer, and K. R. Asmis, *Phys. Chem. Chem. Phys.* **10**, 3992 (2008).
- ⁴⁰G. von Helden, D. van Heijnsbergen, and G. Meijer, *J. Phys. Chem. A* **107**, 1671 (2003).
- ⁴¹M. B. Knickelbein, *Phys. Rev. A* **67**, 013202 (2003).
- ⁴²M. Knickelbein, *J. Chem. Phys.* **102**, 1 (1995).
- ⁴³S. H. Yang and M. B. Knickelbein, *Z. Phys. D: At., Mol. Clusters* **31**, 199 (1994).
- ⁴⁴F. Dong, S. Heinbuch, S. G. He, Y. Xie, J. J. Rocca, and E. R. Bernstein, *J. Chem. Phys.* **125**, 164318/1 (2006).
- ⁴⁵S. Heinbuch, F. Dong, J. J. Rocca, and E. R. Bernstein, *J. Opt. Soc. Am. B* **25**, B85 (2008).
- ⁴⁶S. Heinbuch, F. Dong, J. J. Rocca, and E. R. Bernstein, *Proc. SPIE* **6921**, 69213F (2008).
- ⁴⁷E. R. Bernstein and Y. Matsuda, in *Environmental Catalysis*, edited by V. H. Grassian (CRC press, Boca Raton, FL, 2005), pp. 421.
- ⁴⁸Y. Gong, M. Zhou, and L. Andrews, *Chem. Rev.* **109**, 6765 (2009).
- ⁴⁹M. Pykavy and C. van Wullen, *J. Chem. Phys.* **120**, 4207 (2004).
- ⁵⁰Y. Matsuda and E. R. Bernstein, *J. Phys. Chem.* **109**, 3803 (2005).
- ⁵¹M. Calatayud, J. Andres, and A. Beltran, *J. Phys. Chem. A* **105**, 9760 (2001).
- ⁵²D. R. Justes, R. Mitric, N. A. Moore, V. Bonacic-Koutecky, and A. W. Castleman, Jr., *J. Am. Chem. Soc.* **125**, 6289 (2002).
- ⁵³A. J. Merer, *Annu. Rev. Phys. Chem.* **40**, 407 (1989).
- ⁵⁴M. D. Morse, *Chem. Rev.* **86**, 1049 (1986).
- ⁵⁵D. E. Clemmer, N. F. Dalleska, and P. B. Armentrout, *Chem. Phys. Lett.* **190**, 259 (1992).
- ⁵⁶M. C. R. Cockett, J. M. Dyke, A. M. Ellis, M. Fehér, and T. G. Wright, *J. Electron. Spectrosc. Relat. Phenom.* **51**, 529 (1990).
- ⁵⁷M. C. R. Cockett, L. Nyulászi, T. Veszprémi, T. G. Wright, and J. M. Dyke, *J. Electron. Spectrosc. Relat. Phenom.* **57**, 373 (1991).
- ⁵⁸M. C. R. Cockett, J. M. Dyke, A. M. Ellis, and T. G. Wright, *J. Chem. Soc. Faraday T* **87**, 19 (1991).
- ⁵⁹C. E. Young, R. B. Cohen, P. M. Dehmer, L. G. Pobo, and S. Wexler, *J. Chem. Phys.* **65**, 2562 (1976).
- ⁶⁰L. Andrews, M. Zhou, G. V. Chertihin, and C. W. Bauschlicher, *J. Phys. Chem. A* **103**, 6525 (1999).
- ⁶¹T. K. Todorova, I. Infante, L. Gagliardi, and J. M. Dyke, *J. Phys. Chem. A* **112**, 7825 (2008).
- ⁶²Y. Liu, L. Wu, C. H. Zhang, S. A. Krasnokutski, and D. S. Yang, *J. Chem. Phys.* **135**, 034309 (2011).
- ⁶³D. Proch and T. Trickl, *Rev. Sci. Instrum.* **60**, 713 (1989).
- ⁶⁴C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards, Washington, DC, 1971).

- ⁶⁵M. A. Duncan, T. G. Dietz, and R. E. Smalley, *J. Chem. Phys.* **75**, 2118 (1981).
- ⁶⁶C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- ⁶⁷A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- ⁶⁸M. Head-Gordon, J. A. Pople, and M. J. Frisch, *Chem. Phys. Lett.* **153**, 503 (1988).
- ⁶⁹J. Cizek, in *Advances in Chemical Physics*, edited by P. C. Hariharan (Wiley Interscience, New York, 1969), Vol. 14, p. 35.
- ⁷⁰J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.* **87**, 5968 (1987).
- ⁷¹R. A. Kendall, J. T. H. Dunning, and R. J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992).
- ⁷²R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.* **72**, 650 (1980).
- ⁷³X. Cao and M. Dolg, *J. Chem. Phys.* **115**, 7348 (2001).
- ⁷⁴M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 09, Revision A.1, Gaussian, Inc., Wallingford, CT, 2009.
- ⁷⁵P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.* **115**, 259 (1985).
- ⁷⁶H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **82**, 5053 (1985).
- ⁷⁷P. Celani and H.-J. Werner, *J. Chem. Phys.* **112**, 5546 (2000).
- ⁷⁸B. O. Roos and K. Andersson, *Chem. Phys. Lett.* **245**, 215 (1995).
- ⁷⁹B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov, P.-O. Widmark, and A. C. Borin, *J. Phys. Chem. A* **112**, 11431 (2008).
- ⁸⁰M. Reiher and A. Wolf, *J. Chem. Phys.* **121**, 2037 (2004).
- ⁸¹M. Reiher and A. Wolf, *J. Chem. Phys.* **121**, 10945 (2004).
- ⁸²H.-J. Werner, P. J. Knowles, F. R. Manby, M. Schütz *et al.*, MOLPRO, version 2010.1, a package of *ab initio* programs, 2010, see <http://www.molpro.net>.
- ⁸³D. S. Yang, M. Z. Zgierski, D. M. Rayner, P. A. Hackett, A. Martinez, D. R. Salahub, P. N. Roy, and T. Carrington, *J. Chem. Phys.* **103**, 5335 (1995).
- ⁸⁴A. Berces, M. Z. Zgierski, and D.-S. Yang, *Computational Molecular Spectroscopy* (Wiley, New York, 2000).
- ⁸⁵S. Li, Ph.D. thesis, University of Kentucky, 2004.
- ⁸⁶I. A. M. E. V. Doktorov and V. I. Man'ko, *J. Mol. Spectrosc.* **64**, 302 (1977).
- ⁸⁷F. Duschinsky, *Acta Physicochim. URSS* **7**, 551 (1937).
- ⁸⁸J. F. Fuller, S. Li, B. R. Sohnlein, G. K. Rothschof, and D.-S. Yang, *Chem. Phys. Lett.* **366**, 141 (2002).
- ⁸⁹D. R. Lide, *CRC Handbook of Chemistry and Physics*, 88 ed. (CRC, Boca Raton, 2008).
- ⁹⁰M. E. Jacox, *J. Phys. Chem. Ref. Data* **3**, 1 (1994).
- ⁹¹See <http://webbook.nist.gov/chemistry/> for NIST Standard Reference Database Number 69.
- ⁹²D. S. Yang, *J. Phys. Chem. Lett.* **2**, 25 (2011).
- ⁹³See <http://www.nist.gov/pml/data/asd.cfm> for atomic spectra database.