

Negative ion photoelectron spectroscopy of copper hydrides

Ryan M.D. Calvi, Django H. Andrews, W. Carl Lineberger *

JILA and Department of Chemistry and Biochemistry, 440 UCB, University of Colorado, Boulder, CO 80309-0440, United States

Received 23 April 2007

Available online 23 May 2007

Abstract

We report photoelectron imaging spectra of CuH^- and CuH_2^- and their deuterated analogs. The CuH^- photoelectron spectrum exhibits transitions to the ground ($X^1\Sigma^+$) and lowest excited triplet ($a^3\Sigma^+$) and singlet ($A^1\Sigma^+$) states, with $\text{EA}(\text{CuH})$ 0.444(6) eV. The photoelectron spectrum of linear $X^1\Sigma_g^+$ HCuH^- is dominated by a transition to the linear excited $A^2\Sigma_g^+$ state with a 2.853 eV binding energy. It is accompanied by an extended unresolved vibrational progression involving the bent CuH_2 X^2B_2 ground state. *Ab initio* calculations show a 0.255 eV energy difference between these two states allow determination of $\text{EA}(\text{CuH}_2)$, 2.60(5) eV.

© 2007 Elsevier B.V. All rights reserved.

1. Introduction

Reactions of the form $M + \text{H}_2 \rightarrow \text{MH} + \text{H}$ are important prototypes for the process of hydrogen splitting on transition metals. These reactions can proceed through an intermediate MH_2 . One class of intermediates, the copper hydrides, has been the subject of numerous theoretical and experimental studies. These hydrides are important for understanding the absorption of hydrogen onto metal surfaces in heterogeneous catalysis [1]. As a result, there have been numerous spectroscopic [2–9] and computational [1,8,10–18] studies of copper monohydride, while difficulties in synthesizing copper dihydride have largely limited the investigations to theorists.

Copper monohydride emission and absorption spectra were first observed eighty years ago [3], followed by Ringström's 1966 study [6], in which he characterized five CuH electronic states. Since Ringström, several groups have characterized a number of CuH singlet and triplet states [5,7–9,19–22]. The most recent work was performed by Andrews and co-workers on laser-ablated Cu atoms with hydrogen in low temperature matrices [2,8]. The experimental studies were augmented by increasingly sophisticated calculations of the low-lying states of CuH

[8,11–14,17,23,24]. Notably missing in the experimental work of copper hydride is the lowest triplet state, $a^3\Sigma^+$. This state is a prominent feature of the CuH^- photoelectron spectrum.

Copper dihydride has proven much more difficult to investigate than the monohydride, both experimentally and theoretically. The theoretical difficulties arise from the complex electronic structure of CuH_2 , including bent and linear excited states, conical intersections, and multiple important electronic configurations. Only recently have elaborate calculations begun to provide consistent electronic structures of CuH_2 [12]. Most theoretical work has addressed barriers to CuH_2 formation, CuH_2 energies relative to $\text{Cu}(^2S) + \text{H}_2$ and $\text{CuH} + \text{H}$, adiabatic correlations, and conical intersections [1,2,8,12,15,16]. Theory has shown the ground state lies approximately 0.45 eV above the $\text{Cu}(^2S) + \text{H}_2$ asymptote, with a barrier of about 1.4 eV separating CuH_2 from these constituents [6,7,9,12]. However, calculations have shown the CuH_2 molecule to be unstable with respect to decomposition to $\text{CuH} + \text{H}$.

Andrews and co-workers recently detected infrared absorptions in a hydrogen matrix that they could attribute to CuH_2 and CuH_2^- [2,8]. However, there have been no reports of isolated CuH_2 . Earlier matrix attempts to synthesize copper dihydride only provided evidence for CuH [5]. A major computational finding was the formation of copper dihydride must be accomplished by reacting excited

* Corresponding author. Fax: +1 303 492 8994.

E-mail address: wcl@jila.colorado.edu (W.C. Lineberger).

Cu (2P) atoms and H_2 ($^1\Sigma^+$) molecules to form the metastable 2B_2 intermediate CuH_2^* along the path to ground state (2B_2) CuH_2 [5,11,12,25].

In this Letter, we report the production and photoelectron spectra of CuH^- and CuH_2^- anions, using an apparatus described previously [26]. The CuH_2^- photoelectron spectra give electron affinities of both species, as well as the direct observation of both a previously unobserved linear $HCuH$ intermediate in the hydrogen-splitting reaction and the lowest triplet state of CuH .

2. Experiment

The photoelectron spectroscopy of copper hydrides is carried out using a velocity map imaging photoelectron spectrometer that has been described previously [26]. The sputter ion source gas consists of argon saturated with water vapor at 45 psi. The gas mixture is expanded into the chamber using a pulsed General Valve; the emerging molecular beam initiates a discharge between a copper cathode (-3 kV) and a stainless steel pin, held at ground potential, producing Cu^- anions and small clusters. The anions react with the gas mixture producing CuH^- and CuH_2^- [27]. The ion of interest is mass selected by a time-of-flight mass spectrometer and intersected with a 2 mJ (355 or 600 nm) laser pulse in a velocity map imaging photoelectron spectrometer [26,28]. The three-dimensional photoelectron image is reconstructed using the BASEX inversion algorithm [29]. The photoelectron energy scale is calibrated using well-known Cu^2S , $^2D_{3/2,5/2} \leftarrow Cu^-$ 1S transitions [30]. For electron kinetic energies below 200 meV, electron binding energies can be determined with an accuracy of ± 0.005 eV or better [26].

The interpretation of the experimental results was aided by DFT calculations using the B3LYP method with the 6-311++G(3dp,3df) and SDD basis sets for hydrogen and copper, respectively, utilizing GAUSSIAN 03 [31]. These calculations supplement the extensive earlier theoretical studies [4,5,8,12–14,16]. The optimized geometries and vibrational frequencies of the anion and neutral obtained in these earlier calculations are utilized in Franck–Condon simulations of the photoelectron spectra using the PESCAL program [32]. Only $|\Delta r|$ can be reliably determined from the Franck–Condon simulations; the sign of Δr is obtained from the calculated structures of the anion and neutral.

3. Results and discussion

3.1. CuH and CuD

The CuH $X^1\Sigma^+$ ground state arises from the combination of the Cu $3d^{10}4s^1$ and the H $1s$ orbitals giving a σ^2 bonding HOMO. Adding an additional electron forms the anion in the $^2\Sigma^+$ state, a $\sigma^2\sigma^*$ configuration [13]. The lowest energy excited $a^3\Sigma^+$ state of CuH arises from the triplet coupled $\sigma\sigma^*$ configuration, making both states accessible by single electron photodetachment from $\sigma^2\sigma^*$ $X^2\Sigma^+$

CuH^- . The lowest excited CuH singlet state, $A^1\Sigma^+$, does not arise from this configuration, but rather is formed from the $Cu^* 3d^9 4s^2$ and H $1s$ orbitals, giving rise to a $d^9\sigma^2\sigma^*$ configuration [13], also accessible by photodetachment of a Cu d-electron from CuH^- . The energy difference between the $X^1\Sigma^+$ and $A^1\Sigma^+$ states is well known [6], but the $a^3\Sigma^+$ state has not previously been observed.

Fig. 1 depicts photoelectron spectra of CuH^- recorded at two wavelengths, 600 nm (top trace) and 355 nm (bottom trace); the small Cu^- contamination in the spectrum provides the needed energy scale calibration. The CuH^- photoelectron spectra are completely consistent with the qualitative expectations described above. Comparison of the observed peak separations with the known CuH $A^1\Sigma^+ \leftarrow X^1\Sigma^+$ splitting enables the identification of the transitions shown in Fig. 1.

As the lowest electron kinetic energies are most accurately determined, we derive EA(CuH) from energy of the transition to produce $A^1\Sigma^+$ CuH . The result is EA(CuH) = 0.444(6) eV. Two peaks are seen, corresponding to $v=0$ and 1 of $X^1\Sigma^+$ CuH , with a separation of $1835(50)$ cm^{-1} , in reasonable agreement with the very accurate 1866 cm^{-1} obtained by Brault and Bernath [9]. This short vibrational progression allows the use of the Franck–Condon simulation program to obtain $|\Delta r|(X$ $CuH - X$ $CuH^-) = 0.104(3)$ Å. As the added electron in the anion is antibonding, we obtain $r_e(X$ $CuH^-) = 1.567(3)$ Å.

Measurement of the electron affinity allows for the measurement of the dissociation energy (D_0) of the anion. Utilizing $D_0(CuH) = 2.84(4)$ eV measured by Rao [33] in a thermochemical cycle with EA(CuH) gives $D_0(X$ $CuH^- \rightarrow Cu^- + H) = 2.05(6)$ eV; the weaker anion bond is expected based upon the antibonding character of the added electron. The photoelectron spectrum of CuD^- confirms these assignments.

The peak with the highest binding energy corresponds to the known separation between the ground and the

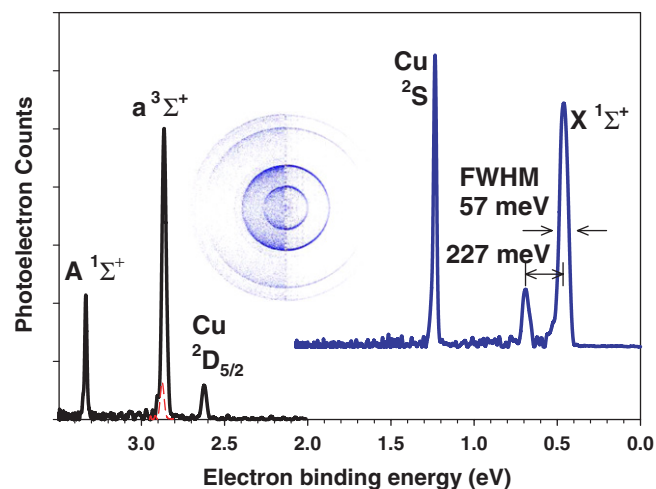


Fig. 1. 355 and 600 nm photoelectron spectra of $^{63}CuH^-$. A 355 nm photoelectron image and reconstruction are also shown.

Table 1
Recommended spectroscopic constants for ^{63}CuH and ^{63}CuD

State	T_{0-0} (eV)	ω_{1-0} (cm^{-1})	r_e (Å)
$^{63}\text{CuH } \mathbf{A}^1\Sigma^+$	2.890 ^b	1610.4 ^c	1.5663 ^g
$^{63}\text{CuH } \mathbf{a}^3\Sigma^+$	2.418(6)*	1762 ^{a,f}	1.567(5) ^{e,*}
$^{63}\text{CuH } \mathbf{X}^1\Sigma^+$	0	1866.4 ^d	1.46263 ^c
$^{63}\text{CuH}^- \mathbf{X}^2\Sigma^+$	-0.444(6)*	1564 ^f	1.567(3)*
$^{63}\text{CuD } \mathbf{A}^1\Sigma^+$	2.892 ^b	1171.9 ^b	1.566(3) ^b
$^{63}\text{CuD } \mathbf{a}^3\Sigma^+$	2.425(6)*	1174 ^{a,f}	1.567(5) ^{e,*}
$^{63}\text{CuD } \mathbf{X}^1\Sigma^+$	0	1346.2 ^c	1.4625(5) ^c
$^{63}\text{CuD}^- \mathbf{X}^2\Sigma^+$	-0.439(6)*	1115 ^f	1.567(3)*

Values marked with an asterisk are obtained from spectra reported in this Letter.

^a Calculated at the CASSCF level by Marian [14].

^b Spectroscopic results from Ringström [6].

^c Reported in Herzberg [34].

^d Measured by Brault and Bernath using Fourier transform emission spectroscopy [9].

^e Based upon non-observation of a $\Delta v = +1$ transition in the photoelectron spectrum.

^f Present B3LYP DFT calculations, with 6-311++G(3dp,3df)/SDD basis sets for hydrogen and copper, respectively.

^g Measured by Bernath in infrared emission spectrum [7].

first-excited singlet state, $\mathbf{A}^1\Sigma^+$ state [6,14]. The photon energy was insufficient to access the $v = 1$ transition, precluding measurement of either the bond length or vibrational frequency. Previous experimental studies give $r_e(\mathbf{A}^1\Sigma^+\text{CuH}) = 1.572$ Å, with $\omega_e = 1610$ cm^{-1} [6,34].

The excitation energy of the $\mathbf{a}^3\Sigma^+$ state, 2.425(6) eV, is determined by measurement of the $\mathbf{A}^1\Sigma^+ - \mathbf{a}^3\Sigma^+$ splitting, compared to ~ 2.29 eV obtained in several calculations [13–15]. A vibrational progression is not observed, indicating that the detached electron was nonbonding and $r_e(\mathbf{a}^3\Sigma^+) = 1.567(5)$ Å, the same as that of the anion. This result compares with the calculated bond length, 1.54 Å [14]. There is a small contribution to this transition from $\text{Cu}^2\text{D}_{3/2}$ (dashed line in Fig. 1), but it does not significantly affect the reported values. Table 1 summarizes our view of the ‘best’ thermochemical values for those states of CuH and CuH^- reported in this Letter, using the present results where appropriate.

3.2. CuH_2 and CuD_2

The ground state of CuH_2 has C_{2v} symmetry with a $(5a_1)^2(3b_2)^1$ orbital configuration, yielding a bent ${}^2\text{B}_2$ state. The lowest energy configuration of the anion is a linear HCuH^- $(3\sigma_g)^2(2\sigma_u)^2$ configuration, giving rise to the $\mathbf{X}^1\Sigma_g^+$ anion ground state. The sputter ion source yields intense beams of CuH_2^- . Electron photodetachment produces both the bent $\mathbf{X}^2\text{B}_2$ CuH_2 and a low lying $\mathbf{A}^2\Sigma_g^+$ excited state with a geometry very similar to that of the anion [12]. Both of these states should be observed in the CuH_2^- photoelectron spectrum, the ground state with extensive, poorly resolved vibrational progressions, and the excited state with a sharp, near diagonal transition. These qualitative expectations are exactly what is observed for CuD_2^- , as seen in Fig. 2.

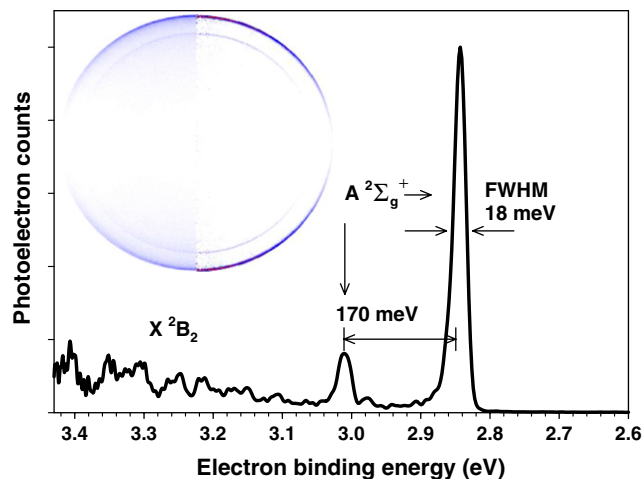


Fig. 2. 355 nm photoelectron spectrum of $^{65}\text{CuD}_2^-$ showing the near diagonal transition to $\mathbf{A}^2\Sigma_g^+$ and the extended unresolved vibrational progression in the $\mathbf{X}^2\text{B}_2$ ground state. The corresponding image and B3LYP reconstruction appear as an inset.

The photoelectron spectrum is dominated by a strong transition to the excited $\mathbf{A}^2\Sigma_g^+$ state of CuD_2 . A short progression in the symmetric stretch mode is observed with a frequency of 1370(40) cm^{-1} ; the assignment to a vibrational progression was confirmed by hydrogen substitution. Calibrating the energy scale with the nearly isoenergetic $\text{Cu}^-1\text{S} \rightarrow \text{Cu}^2\text{D}_{3/2}$ transition, we find the binding energy of the $\mathbf{A}^2\Sigma_g^+$ state of CuD_2 to be 2.841(5) eV. Photoelectron ejection is strongly peaked parallel to the laser polarization vector, with an anisotropy β of 1.8(1), consistent with photodetachment removing an electron from the $3\sigma_g$ orbital in the anion [10–12]. The short vibrational progression allows a harmonic Franck–Condon intensity analysis, showing $|\Delta r(\text{Cu–H})| = 0.04$ Å. Our DFT calculations show the anion to have the longer Cu–H bond length, providing the sign associated with $|\Delta r(\text{Cu–H})|$ above. As $\mathbf{A}^2\Sigma_g^+ \text{CuH}_2$ has not been previously observed, we employ the much higher level $\mathbf{A}^2\Sigma_g^+ \text{CuH}_2$ bond length calculated by Chambaud (1.52 Å, [12]) to obtain the anion bond length in the anion as 1.56(2) Å.

The extended, unresolved progression that is present in the spectrum arises from transitions to high vibrational levels in the ${}^2\text{B}_2$ ground state, and the extent of the progression arises from the large geometry difference between the linear anion and the bent neutral ground state. Calculations by Chambaud [12] place the ${}^2\text{B}_2$ ground state ~ 0.2 eV below the $\mathbf{A}^2\Sigma_g^+$ state, at least 0.3 eV below the binding energy where we first observe the extended progression. We cannot quantitatively simulate this progression, for the potential energy surfaces are too poorly known to obtain vibrational energy levels in the bent, linear and transition regions; moreover, the experimental spectra exhibit no clear vibrational peaks, and even a vertical detachment energy cannot be obtained from the data. Nevertheless, the extended vibrational progression is consistent with the large predicted geometry change. If we use the calculated geometries for both states, employ

harmonic vibrational frequencies, and assumes the electronic transition matrix element are the same for both ground and excited states, then we obtain the simulation shown in Fig. 3. The only point to this qualitative CuH₂ X²B₂ simulation is that both the absence of signal at the ²B₂ origin (2.6 eV) and the intensity of the extended progression in the energy range observed are consistent with expectations.

While we cannot resolve transitions in the extended vibrational progression in the ground state of copper dihydride, we can obtain EA(CuH₂) as the difference between the measured electron binding energy of HCuH A²Σ_g⁺ (2.853(5) eV) and the calculated separation between the A²Σ_g⁺ state and CuH₂ X²B₂ ground state (0.255 eV) [12]. This energy difference is obtained from Chambaud's MRCISD calculation of the splitting between these states

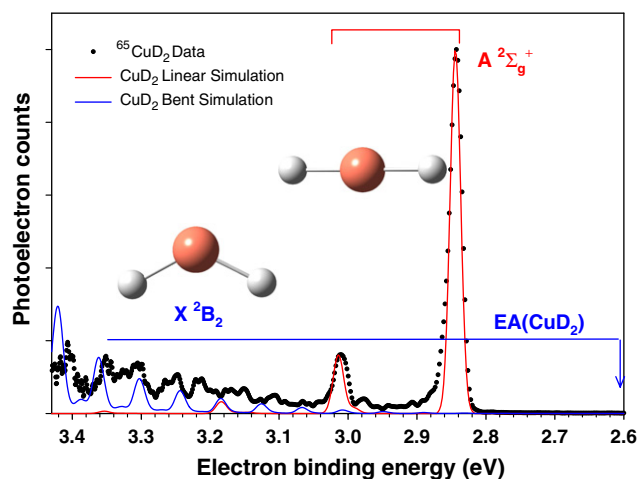


Fig. 3. Comparison of the photoelectron spectrum of CuD₂ with the simulated spectrum. The large geometry difference between the linear anion and bent ground state means that there will be no detectable photoelectron signal at EA(CuD₂) (vertical arrow). The simulation does not consider the major effects of the bent → linear transition, and must be considered as being very qualitative.

(0.192 eV), increased by 63 meV to account for zero point energies in both states, using the Chambaud's CuH₂ X and A state harmonic frequencies [12]. If we estimate the uncertainty in the calculation to be 20%, 0.05 eV, then we obtain EA(CuH₂) = 2.60(5) eV. This mixing of measured and calculated energies is largely justified by the fact that the measured energy is an order of magnitude larger than the calculated correction used to obtain the electron affinity. Similarly, we find EA(CuD₂) = 2.60(5) eV. Table 2 summarizes our view of the 'best' thermochemical values for those states of CuH₂ and CuH₂⁻ reported in this Letter, using the present results where appropriate.

This determination of EA(CuH₂) allows an estimate of the anion dissociation energy, using a similar mix of calculated and measured energies, once again justified by the fact that the theoretically determined quantities make a much smaller contribution to the dissociation energy than do the experimental ones. Chambaud reports $D_e(\text{CuH}_2 \text{ X}^2\text{B}_2 - \text{CuH} + \text{H}) = 1.32 \text{ eV}$ [12]. Again, zero point corrections reduce D_0 to 1.05 eV. Here we crudely estimate that the error in the calculated dissociation energy might be 0.2 eV. This dissociation energy, coupled with the electron affinities of CuH and CuH₂, form a thermochemical cycle to give $D_0(\text{HCuH}^- \rightarrow \text{CuH}^- + \text{H}) = 3.2(2) \text{ eV}$. This bond is much stronger in the anion than in the ground state of the neutral molecule. Since we know from the first study that $D_0(\text{CuH}^- \rightarrow \text{Cu}^- + \text{H}) = 2.05(6) \text{ eV}$, this result also allows us to conclude that removing the first hydrogen atom from HCuH⁻ is significantly harder than removing the second one.

4. Conclusion

The use of a sputter discharge ion source has allowed the production of copper monohydride and dihydride anions. The negative ion velocity map imaging photoelectron spectra provide quantitative electron binding energies and dissociation energies, yielding new insight into the bonding

Table 2
Recommended spectroscopic constants for ⁶⁵CuD₂ and ⁶⁵CuH₂

State	Electron binding energy (eV)	ν (cm ⁻¹)				H–Cu–H r_e (Å)
		ν_1	ν_2	ν_3	ν_4	
⁶⁵ CuD ₂ A ² Σ _g ⁺	2.841(5) ^a	592.8 ^c	592.8 ^c	1211 ^e	1370(40) [*]	1.52 ^a
⁶⁵ CuD ₂ X ² B ₂	2.60(5) ^b	1196 ^c	(458.5 ^c)	1291 ^e		1.468 ^a
⁶⁵ CuD ₂ ⁻ X ¹ Σ _g ⁺	0 [*]	470 ^c	470 ^c	1065 ^e	1107.3 ^c	1.56(3) [*]
⁶⁵ CuH ₂ A ² Σ _g ⁺	2.853(5) ^a	817 ^f	817 ^f	1808 ^f	1880(40) [*]	1.52 ^a
⁶⁵ CuH ₂ X ² B ₂	2.60(5) ^a	1935 ^c	636.5 ^c (685 ^d)	1799 ^d		1.468 ^a
⁶⁵ CuH ₂ ⁻ X ¹ Σ _g ⁺	0 [*]	655 ^c	655 ^c	1065 ^e	1517.8 ^c	1.56(3) [*]

Values marked with an asterisk are obtained from spectra reported in this Letter.

^a From Chambaud X–A separation, MRCISD [12] and the experimental A state binding energy.

^b Chambaud [12], X–A separation as above, corrected for H–D zero point differences, using calculated harmonic CuH₂ vibrational energies.

^c IR absorption in a hydrogen matrix [8].

^d Chambaud anharmonic frequencies calculated at the MRCISD level [12].

^e Present B3LYP DFT calculations with 6-311++G(3dp,3df)/SDD basis sets for hydrogen and copper, respectively.

^f MP2-MP4 calculations performed by Fitzpatrick [16].

and structure of these small molecules. The ion production technique employed here will be useful for studies of other transition metal hydrides, and may provide new insights into the use of transition metals for hydrogen splitting processes.

Acknowledgements

This work was supported by the National Science Foundation and the Air Force Office of Scientific Research.

References

- [1] P.E.M. Siegbahn, M.R.A. Blomberg, C.W. Bauschlicher Jr., *J. Chem. Phys.* 81 (1984) 1373.
- [2] L. Andrews, X.F. Wang, *J. Am. Chem. Soc.* 125 (2003) 11751.
- [3] R. Frerichs, *Z. Phys.* 20 (1923) 170.
- [4] J. Niu, B.K. Rao, P. Jena, M. Manninen, *Phys. Rev. B* 51 (1995) 4475.
- [5] G.A. Ozin, C. Gracie, *J. Phys. Chem.* 88 (1984) 643.
- [6] U. Ringström, *Ark. Fys.* 32 (1966) 211.
- [7] J.Y. Seto, Z. Morbi, F. Charron, S.K. Lee, P.F. Bernath, R.J. Le Roy, *J. Chem. Phys.* 110 (1999) 11756.
- [8] X.F. Wang, L. Andrews, L. Manceron, C. Marsden, *J. Phys. Chem. A* 107 (2003) 8492.
- [9] R.S. Ram, P.F. Bernath, J.W. Brault, *J. Mol. Spectrosc.* 113 (1985) 269.
- [10] J. García-Prieto, M.E. Ruiz, O. Novaro, *J. Am. Chem. Soc.* 107 (1985) 5635.
- [11] J. García-Prieto, M.E. Ruiz, E. Poulain, G.A. Ozin, O. Novaro, *J. Chem. Phys.* 81 (1984) 5920.
- [12] M. Guitou-Guichemerre, G. Chambaud, *J. Chem. Phys.* 122 (2005) 204325-11.
- [13] M. Hliwa, J.C. Barthelat, M. Pelissier, F. Spiegelmann, *Chem. Phys. Lett.* 132 (1986) 205.
- [14] C.M. Marian, *J. Chem. Phys.* 94 (1991) 5574.
- [15] M.T. Nguyen, M.A. McGinn, N.J. Fitzpatrick, *J. Chem. Soc., Faraday Trans. 2* 82 (1986) 1427.
- [16] M.T. Nguyen, M.A. McGinn, N.J. Fitzpatrick, *J. Chem. Soc., Faraday Trans. 2* 82 (1986) 69.
- [17] R. Pouamerigo, M. Merchan, I. Nebotgil, P.A. Malmqvist, B.O. Roos, *J. Chem. Phys.* 101 (1994) 4893.
- [18] M.E. Ruiz, J. García-Prieto, O. Novaro, *J. Chem. Phys.* 80 (1984) 1529.
- [19] C.M. Brown, M.L. Ginter, *J. Mol. Spectrosc.* 80 (1980) 145.
- [20] W. Fernando, L.C. O'Brien, P.F. Bernath, *J. Mol. Spectrosc.* 139 (1990) 461.
- [21] T.D. Varberg, K.M. Evenson, *J. Mol. Spectrosc.* 164 (1994) 531.
- [22] S.P. Beaton, K.M. Evenson, *J. Mol. Spectrosc.* 142 (1990) 336.
- [23] E.G. Para, E. Martinez, J.M. Alvarino, *J. Quant. Spectrosc. Radiat. Transfer* 30 (1983) 439.
- [24] F. Castano, J. Dejuan, E. Martinez, *Spectrochim. Acta A: Mol. Biomol. Spectrosc.* 38 (1982) 545.
- [25] G.A. Ozin, J.G. McCaffrey, D.F. McIntosh, *Pure Appl. Chem.* 56 (1984) 111.
- [26] G.J. Rathbone, T. Sanford, D. Andrews, W.C. Lineberger, *Chem. Phys. Lett.* 401 (2005) 570.
- [27] F. Muntean, M.S. Taylor, A.B. McCoy, W.C. Lineberger, *J. Chem. Phys.* 121 (2004) 5676.
- [28] A. Eppink, D.H. Parker, *Rev. Sci. Instrum.* 68 (1997) 3477.
- [29] V. Dribinski, A. Ossadtchi, V.A. Mandelshtam, H. Reisler, *Rev. Sci. Instrum.* 73 (2002) 2634.
- [30] R.C. Bilodeau, M. Scheer, H.K. Haugen, *J. Phys. B: At. Mol. Opt. Phys.* 31 (1998) 3885.
- [31] M.J. Frisch et al., GAUSSIAN 03, Gaussian Inc., Pittsburgh PA, 2003.
- [32] K.M. Ervin, T.M. Ramond, G.E. Davico, R.L. Schwartz, S.M. Casey, W.C. Lineberger, *J. Phys. Chem. A* 105 (2001) 10822.
- [33] V.M. Rao, M.L.P. Rao, P.T. Rao, *J. Quant. Spectrosc. Radiat. Transfer* 25 (1981) 547.
- [34] K. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure, Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1979.