Photoelectron and threshold photoelectron valence spectra of pyridine

Malgorzata A. Smialek, Michael A. MacDonald, Sylwia Ptasińska, Lucia Zuin, and Nigel J. Mason

1 Department of Control and Power Engineering, Faculty of Ocean Engineering and Ship Technology, Gdansk University of Technology, Gabriela Narutowicza 11/12, 80-233 Gdansk, Poland
2 Canadian Light Source Inc., 44 Innovation Boulevard, Saskatoon SK S7N 2V3, Canada
3 Radiation Laboratory and Department of Physics, University of Notre Dame, Notre Dame, IN 46556, USA
4 Department of Physical Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK

Received 26 November 2015 / Received in final form 22 December 2015
Published online 25 February 2016
© The Author(s) 2016. This article is published with open access at Springerlink.com

Abstract. The pyridine molecule has been examined by the means of photoelectron and threshold photoelectron spectroscopies. Ionization energies were determined for both outer and inner valence orbitals and new adiabatic values were also resolved. Vibronic structure associated with several states was assigned mainly to be due to C–C stretches and ring bends. Additionally, a Rydberg state converging to 7b state was ascribed. The data shown here are in a good agreement with previous results and brings some new insights into the electronic structure of this biologically and astrochemically relevant and important molecule.

1 Introduction

Pyridine molecule, shown in Figure 1, was chosen as the subject of this study. This molecule is often used as a precursor to agrochemicals (bacteri- and herbicides) and medicines (sulfapyridine or tripelemamine) [1] and also utilized as a solvent or chemical reagent [2]. Many chemicals contain pyridine ring structure, like B-group vitamins or nicotine [3]. Investigations of this molecule are thus not only important due to its industrial or biological implications but are also valid for astrochemistry, since it has been shown that B-group vitamins [4] can be found on the surface of meteorites [5].

This simple aromatic azabenzene has been extensively studied in the past with respect to both its vibrational [6–8] and electronic structure [9] by experimental [10–14] and computational [15–18] approaches. Moreover, low-lying Rydberg states have also been examined for this molecule [19,20]. From the abovementioned studies it was concluded that the HOMO in pyridine is of n-type. Introducing the nitrogen atom into the benzene ring causes perturbation in the energy levels and thus some new transitions are available in pyridine that are due to the lone-pair electrons [13,21].

Fig. 1. Pyridine molecule; gray indicates carbon atoms, blue indicates nitrogen substituting one of the methine groups of benzene ring.

Also, photoionization and fragmentation of this molecule have been studied in the 8–30 eV range indicating that there is a significant bond rearrangement and nuclear motion during dissociation, since relative fragment yields formed upon varying excitation energy differ significantly [22]. Recently, it was found that dissociation of pyridine may occur via ring opening and isomerization mechanisms [23].

In this work we focused on photoelectron (PES) and threshold photoelectron (TPES) spectroscopic studies of the pyridine molecule. Using a high resolution photoelectron spectrometer, described later, it was possible not only to resolve the inner and outer valence ionization energies, but also, throughout the threshold electron measurements, confirm the vibronic structure associated with most of the bands in the spectrum.
Fig. 2. Complete valence shell photoelectron spectra of pyridine recorded at (top) thresholds and (bottom) 80 eV incident photon energy; the insert in PES shows 33–65 eV binding energy range, obtained at 100 eV incident photon energy; see text for further details.

2 Materials and methods

2.1 Pyridine sample

Pyridine sample of purity higher than 99.9% was purchased from Sigma-Aldrich, Canada, and used with no further processing. In order to introduce the sample into the UHV system, pyridine (liquid) was transferred into a stainless steel container and degassed in four freeze-thaw-pump cycles.

2.2 Threshold and photoelectron spectra

Both the threshold photoelectron and photoelectron spectra of pyridine (Fig. 2) were recorded at the VLS-PGM beamline [24], at the Canadian Light Source facility in Saskatoon, Canada, using a Double Toroidal Coincidence Spectrometer. The apparatus was described previously in detail [25] and a specific description of the operation in the threshold mode was also provided [26]. Although it was primarily designed to be used for measurements of noble gases and small, diatomic molecules, it was recently proven that it may also be used for measurements on more complicated systems, such as pyrimidine and of its heavier derivatives [27] or esters [28,29].

Briefly, a photoelectron-photoelectron coincidence spectrometer allows for the two electrons, of specified energies, to be detected over a wide range of emission angles. The spectrometer is based on a toroidal geometry and has properties ideally suited for measuring electron angle distributions, since toroidal analysers can be made to energy-select the photoelectrons while preserving the initial angle of emission. The spectrometer consists of two toroidal analysers, each focused on the interaction region. One collects electrons over an azimuthal range of 180°, the other over 120°. These electrostatic analysers are independent, i.e., they are able to detect dissimilar electron energies, with different resolutions.

For photoelectron spectra measurements, both analysers were set to a pass energy of 4 eV. The analysis was performed for the data collected by the 180° toroidal detector. Spectra shown here were calibrated against the $X^2\Sigma_g^+$, $\nu' = 0$ and $A^2\Pi_u$, $\nu' = 0$ peaks of N$_2$, rounded to three decimal places [30,31], introduced to the chamber together with the pyridine sample. The measured resolution from the nitrogen calibration spectra was 60 meV. The photoexcitation energy for the photoelectron spectrum presented here was 80 eV in the 0–33 eV region and 100 eV for 33–65 eV photoelectrons, recorded with the entrance and exit slits of the VLS-PGM beamline set at 50 μm.

For the threshold photoelectron spectra measurements only the 120° toroidal detector was used. The detector was set to collect near-zero-eV electrons and the resolution was determined against the Ar $^2P_{3/2}$ and $^2P_{1/2}$ lines to yield 7 meV. Spectra were normalized to the incident photon flux. No evidence of significant higher order contamination in the TPES spectra was seen. Specifically, there is no vibrationally-resolved structure above 20 eV, which would be reflected in the nominal PES around 10 eV.
3 Results and discussion

From the photoelectron spectrum shown in Figure 2 it was possible to assign all the ionization energies for the inner and outer valence orbitals of the pyridine molecule. The adiabatic and vertical values were obtained through the Gaussian function fitting procedure and are summarized in Table 1, together with the values obtained from the literature. The fitting was performed using Origin Pro 2015 software and the obtained results were at the level of 10% with respect to the values of residuals. Vertical values are marked with lines on the PES spectra in Figures 3–7, bottom panels. The nomenclature for labelling the states are marked with lines on the PES spectra in Figures 3–7, bottom panels. The nomenclature for labelling the states followed that proposed by Clementi [9], although various authors have different recommendations for the order of the molecular orbitals (see for example Moghaddam et al. [17]). The data presented here is not only in an excellent agreement with the previous results, but also, due to high resolution of present experiment, it was possible to assign some new adiabatic ionization energies and resolve bands that previously appeared as one feature.

This was achieved with assistance of measured TPES, shown in Figures 2–7 in the top panels. TPES measurements allowed resolving the vibronic structure associated with most of the ionization energies as well as to assign a possible Rydberg state. These assignments are shown in Figures 3–7 and summarised in Tables 2–4.

A very thorough review by Innes et al. [32] on azabenzenes gives a summary of 27 fundamental vibrational frequencies that can be assigned in pyridine spectrum. From there, Reineck et al. concluded that in the photoelectron spectrum, only the fully symmetric vibrational modes are expected to be strongly excited, and thus only ten of them are of potential interest. In our spectra we also found the series that could not have been assigned to those ten modes due to discrepancies in energy values, therefore, we also used assignments proposed by Partial Urena et al. [7]. In their work additional combinations of vibrational modes were assigned. Table 2 shows the vibrational modes assigned in the spectra presented here (marked in bold in the text).

Over the first band, that consists of the 11a1 and 1a2 states it was possible to ascribe a rich vibronic structure associated with the first IE to a combination of modes: 1 (C–C stretch) and 6a (in-plane ring bend). It should be noted that the obtained values of electron binding energy for all higher electronic states are in an excellent agreement with values given by Reineck et al. [12] and those of Liu et al. [14] that were obtained by a sophisticated photoelectron imaging spectrometer. Also, the value of adiabatic ionization energy, 9.197 eV, is in an excellent agreement with values reported by Liu et al. [14] (9.199 eV), Reineck et al. [12] (9.197 eV) and Riese et al. [33] (9.198 eV). The latter obtained this value through mass-ionized threshold ionization spectroscopy studies.

The position of the vertical ionization energy of the second electronic state of the ion was assigned to be 9.855 eV and also one quantum of the 1 mode can be distinguished on the shoulder of the band.

| Orbital 11aa | 9.550 | 9.855 |
| Orbital 1ab | 9.550 | 9.855 |
| Orbital 2 | 10.583 | 10.583 |
| Orbital 3 | 10.85 | 10.85 |
| Orbital 4 | 12.26 | 12.26 |
| Orbital 5 | 12.999 | 12.999 |

**Table 1. Assignment of bands and their experimental vertical energies obtained from PES of pyridine together with calculated ionization energies (all in eV); second row – adiabatic values.**

*From there, Reineck et al. concluded that in the photoelectron spectrum, only the fully symmetric vibrational modes are expected to be strongly excited, and thus only ten of them are of potential interest. In our spectra we also found the series that could not have been assigned to those ten modes due to discrepancies in energy values, therefore, we also used assignments proposed by Partial Urena et al. [7]. In their work additional combinations of vibrational modes were assigned. Table 2 shows the vibrational modes assigned in the spectra presented here (marked in bold in the text). Over the first band, that consists of the 11a1 and 1a2 states it was possible to ascribe a rich vibronic structure associated with the first IE to a combination of modes: 1 (C–C stretch) and 6a (in-plane ring bend). It should be noted that the obtained values of electron binding energy for all higher electronic states are in an excellent agreement with values given by Reineck et al. [12] and those of Liu et al. [14] that were obtained by a sophisticated photoelectron imaging spectrometer. Also, the value of adiabatic ionization energy, 9.197 eV, is in an excellent agreement with values reported by Liu et al. [14] (9.199 eV), Reineck et al. [12] (9.197 eV) and Riese et al. [33] (9.198 eV). The latter obtained this value through mass-ionized threshold ionization spectroscopy studies.

The position of the vertical ionization energy of the second electronic state of the ion was assigned to be 9.855 eV and also one quantum of the 1 mode can be distinguished on the shoulder of the band.*
Fig. 3. Valence shell photoelectron spectra of pyridine recorded at (top) thresholds and (bottom) 80 eV incident photon energy in the energy range of 9–11 eV.

Table 2. Vibrational modes (Wilson’s notation) [7,32] and their energies found in the pyridine spectrum.

| Mode    | Description                          | Energy (meV) |
|---------|--------------------------------------|--------------|
| 16b     | out-of-plane ring bend               | 31           |
| 16a     | out-of-plane ring bend               | 41           |
| 6a      | in-plane ring bend                   | 70           |
| 1       | carbon-carbon stretch                | 116          |
| 18a     | in-plane C–H bend                    | 152          |
| 14      | carbon-carbon stretch                | 161          |
| 8a      | carbon-carbon stretch                | 204          |
| (16a+3) | out-of-plane ring bend with in-plane C–H bend | 214 |
| (8a+12) | C–C stretch with in-plane ring bend  | 240          |

On the third electronic state of the ion, 2b₁, a combination of 16a (both out-of-plane ring bend) and 6a modes was resolved, with the adiabatic value found at 10.315 eV.

The feature visible only in the TPES, centred at the 11.325 eV, marked in Figure 2 (top) with an arrow, can be assigned to a 4s Rydberg state, converging to the 7b₂ ionization energy. The quantum defect, δ = 0.74, is within the same range with the value obtained by others for the ns transitions converging to the 11a₁ state (δ = 0.85) [20].

In Figure 4 the band consisting of four ionization energies: 7b₂, 1b₁, 10a₁ and 6b₂, is presented. Additionally, in the band of 7b₂ state, a vibronic structure consisting of combination of mode 8 (C–C stretch) with modes 18a (in-plane CH bend) and 6a can be resolved. These results are also in a good agreement with the ones shown previously [12]. Over the 1b₁ band, three quanta of mode 1 can be seen in both the PES and TPES spectra. The adiabatic ionization energies found for these two states yielded 12.262 eV and 12.999 eV, respectively. For the 10a₁ and

Fig. 4. Valence shell photoelectron spectra of pyridine recorded at (top) thresholds and (bottom) 80 eV incident photon energy in an energy range of 12–15 eV.
Table 3. Binding energies of Rydberg and vibrational assignments of bands in pyridine spectrum.

| Binding energy (eV) | Assignment | Utsunomiya et al. [11] | Reineck et al. [12] | Liu et al. [14] |
|---------------------|------------|------------------------|---------------------|-----------------|
| 11a₁ (Fig. 3)       |            |                        |                     |                 |
| 9.199               | 0–0        | –                      | 9.197               | 9.199           |
| 9.276               | 6a         | 9.26                   | 9.271               | 9.273           |
| 9.318               | 1          | –                      | 9.319               | 9.318           |
| 9.348               | 6a²        | 9.36                   | 9.346               | 9.348           |
| 9.393               | 1+6a       | –                      | 9.391               | 9.3925          |
| 9.419               | 6a³        | –                      | 9.421               | 9.419           |
| 9.428               | 1³         | 9.46                   | –                   | 9.428           |
| 9.466               | 1+6a²      | –                      | 9.465               | 9.467           |
| 9.504               | 1²+6a      | –                      | –                   | 9.504           |
| 9.540               | 1+6a³      | –                      | 9.536               | 9.541           |
| 9.555               | 1⁵         | 9.56                   | –                   | 9.555           |
| 9.577               | 1²+6a²     | –                      | 9.580               | 9.579           |
| 9.608               | 1+6a⁴      | –                      | 9.608               | 9.610           |
| 9.656               | 1²+6a³     | 9.66                   | 9.657               | 9.644           |
| 1a₂ (Fig. 3)        |            |                        |                     |                 |
| 9.855               | Vertical IE| 9.80                   | 9.85                | –               |
| 9.977               | 1          | 9.90                   | 9.97                | –               |
| 2b₁ (Fig. 3)        |            |                        |                     |                 |
| 10.351              | 0–0        | –                      | –                   | –               |
| 10.356              | 16a        | –                      | –                   | –               |
| 10.385              | 6a         | –                      | –                   | –               |
| 10.425              | 6a+16a     | –                      | –                   | –               |
| 10.455              | 6a²        | –                      | –                   | –               |
| 10.496              | 6a²+16a    | –                      | –                   | –               |
| 10.522              | 6a³        | –                      | –                   | –               |
| 10.566              | 6a³+16a    | –                      | –                   | –               |
| 10.594              | 6a⁴        | –                      | –                   | –               |
| 10.636              | 6a³+16a    | –                      | –                   | –               |
| 10.663              | 6a⁵        | –                      | –                   | –               |
| 10.699              | 6a²+16a    | –                      | –                   | –               |
| 10.733              | 6a⁶        | –                      | –                   | –               |
| 10.770              | 6a⁶+16a    | –                      | –                   | –               |
| 10.801              | 6a⁷        | –                      | –                   | –               |
| 10.841              | 6a⁷+16a    | –                      | –                   | –               |
| 7b₂ (Fig. 4)        |            |                        |                     |                 |
| 11.325 (Fig. 2)     | 4s(7b₂), δ = 0.74| – | – | – |
| 12.262              | 0–0        | –                      | 12.285              | –               |
| 12.332              | 6a         | –                      | 12.349              | –               |
| 12.401              | 18a        | –                      | 12.392              | –               |
| 12.463              | 8a         | –                      | 12.478              | –               |
| 12.529              | 8a+6a      | –                      | 12.549              | –               |
| 12.602              | 8a+18a     | –                      | 12.580              | –               |
| 12.667              | 8a²        | –                      | –                   | –               |
| 12.736              | 8a²+6a     | –                      | –                   | –               |
| 12.802              | 8a²+18a    | –                      | –                   | –               |
| 12.875              | 8a³        | –                      | –                   | –               |
| 12.946              | 8a³+6a     | –                      | –                   | –               |
| 1b₁ (Fig. 4)        |            |                        |                     |                 |
| 12.999              | 0–0        | –                      | 13.081              | –               |
| 13.114              | 1²         | –                      | 13.207              | –               |
| 13.219              | 1³         | –                      | 13.317              | –               |
| 13.324              | 1³         | –                      | –                   | –               |
Table 4. Binding energies of vibrational assignments of bands in pyridine spectrum; asterisks marks tentative assignments, star marks a combined mode from reference [7].

| Binding energy (eV) | Assignment |
|--------------------|------------|
| 5b\(_2\) (Fig. 5)  | 0–0        |
| 15.247             | 16b        |
| 15.563             | 16b\(^2\)  |
| 15.601             | 16b\(^2\)  + 14 |
| 15.726             | 16b\(^3\)  |
| 15.762             | 16b\(^3\)  + 14 |
| 9a\(_1\) (Fig. 5)  | Vertical IE |
| 15.871             | (8a + 12)\((\star)\) |
| 16.703             | 0–0        |
| 16.938             | (8a + 12)\((\star)\) |
| 17.062             | (8a + 12) + 1\((\star)\) |
| 17.168             | (8a + 12)\(^2\)(\((\star)\) |
| 17.403             | (8a + 12)\(^3\)(\((\star)\) |
| 7a\(_1\) (Fig. 6)  | 0–0        |
| 18.789             | (16a + 3)\((\star)\) |
| 19.043\(*\)        | (16a + 3)\(^2\)(\((\star)\) |
| 19.257\(*\)        | (16a + 3)\(^3\)(\((\star)\) |
| 19.468             | (16a + 3)\(^4\)(\((\star)\) |
| 19.684             | (16a + 3)\(^5\)(\((\star)\) |
| 19.896             | (16a + 3)\(^6\)(\((\star)\) |
| 20.109             | (16a + 3)\(^7\)(\((\star)\) |

6b\(_2\) states it was only possible to obtain the vertical values of 13.796 eV and 14.561 eV, respectively.

There are two bands shown in Figure 5. In the first one, two ionization energies from orbitals 5b\(_2\) and 9a\(_1\) can be distinguished. Further, a mode 16b (out-of-plane ring bend) combined with one quantum of mode 14 (C–C stretch) was resolved over 5b\(_2\) state. This structure was not resolved previously and provided an adiabatic value for ionization of 15.247 eV. The ionization from the 9a\(_1\) state can be associated with one mode of (8a + 12) that is an in-plane ring bend associated with a C–C stretch, according to the findings of Partal Urena et al. [7]. The second band is due to ionization from 8a\(_1\) orbital. The ionization energy in this band is accompanied by three quanta of the combined (8a + 12) mode and one quantum of mode 1. Here, it was also possible for the first time to assign the adiabatic value for ionization from the 8a\(_1\) orbital of 16.703 eV.

In Figure 6 there is only one band that is due to two ionization energies from the orbitals 7a\(_1\) and 4b\(_2\). There is also a vibronic progression associated with the former that can be attributed to six quanta of a combined mode (16a + 3), which is an out-of-plane ring bend mixed with in-plane CH bend. Thus, it was possible to assign an adiabatic value of 18.789 eV for the 7a\(_1\) state, whereas for the 4b\(_2\) only the vertical value of 20.247 eV could be established.

A broad double peak, seen in Figure 7, was determined to be a result of ionization from the 6a\(_1\) and 3b\(_2\) orbitals with vertical values of 23.264 eV and 24.118 eV, respectively. There are also additional two peaks visible in the PES in Figure 7. The first one is due to ionization from the 5a\(_1\) orbital at 28.122 eV. As it was shown through computational methods [18], the features observed in the PES above the binding energy of 25 eV are strongly influenced by multielectron processes (MEP) and thus we ascribed the band centered around 31.2 eV to be due to such interactions. A slight increase in the photoionization efficiency at this energy was also observed by others [34]. In the TPES there are other distinguished features in the range of 29–31 eV that were attributed to the pressure fluctuations during this measurement.
4 Conclusions

In this work we revisited on the subject of photoelectron spectroscopy investigations of the pyridine molecule. Using a high resolution photoelectron spectrometer, it was possible not only to resolve the inner and outer valence ionization energies, but also, throughout the threshold electron measurements, confirm the vibronic structure associated with most of the bands in the spectrum. This vibronic structure associated with several states was assigned mainly to be due to C–C stretches and ring bends. Additionally, a possible Rydberg state, converging to 7b2 state, was ascribed. The data shown here are in an excellent agreement with previous results and brings some new insights into the electronic structure of pyridine molecule.

Research described in this paper was performed at the Canadian Light Source, which is supported by the Canada Foundation for Innovation, Natural Sciences and Engineering Research Council of Canada, the University of Saskatchewan, Western Economic Diversification Canada, the National Research Council Canada, and the Canadian Institutes of Health Research.

References

1. W. M, Arch. Dermatol. 87, 489 (1963)
2. J. Jankolovits, J.W. Kampf, V.L. Pecoraro, Inorg. Chem. 53, 7534 (2014)
3. R.T. Burns, J.A. Pechenik, W.J. Biggers, G. Scavo, C. Lehman, PLoS One 9, e109535 (2014)
4. H. Waisman, C. Elvehjem, Ind. Eng. Chem. Anal. Ed. 13, 221 (1941)
5. P.G. Stoks, A.W. Schwartz, Geochim. Cosmochim. Acta 45, 563 (1981)
6. T. Klots, Spectrochim. Acta Part A 54, 1481 (1998)
7. F. Partal Urena, M. Fernández Gómez, J. López González, E. Martínez Torres, Spectrochim. Acta Part A 59, 2815 (2003)
8. M. Szafra, J. Koput, J. Mol. Struct. 565–566, 439 (2001)
9. E. Clementi, J. Chem. Phys. 46, 4731 (1967)
10. R. Geiter, E. Heilbronner, V. Hornung, Helv. Chim. Acta 55, 255 (1972)
11. C. Utsunomiya, T. Kobayashi, S. Nagakura, Bull. Chem. Soc. Jpn 51, 3482 (1978)
12. I. Reineck, R. Maripuu, H. Veenhuizen, L. Karlsson, K. Siegbahn, M. Powar, W.N. Zu, J.M. Rong, S. Al-Shamma, J. Electron Spectrosc. Relat. Phenom. 27, 15 (1992)
13. I. Walker, M. Palmer, A. Hopkirk, Chem. Phys. 141, 365 (1990)
14. S.Y. Liu, K. Alnama, J. Matsumoto, K. Nishizawa, H. Kohguchi, Y.P. Lee, T. Suzuki, J. Phys. Chem. A 115, 2953 (2011)
15. W. von Niessen, G. Diercksen, L. Cederbaum, Chem. Phys. 10, 345 (1975)
16. D.A. Case, M. Cook, M. Karplus, J. Chem. Phys. 73, 3294 (1980)
17. M.S. Moghaddam, A. Bawagan, K. Tan, W. von Niessen, Chem. Phys. 207, 19 (1996)
18. J.W. Hada, M. Ehara, H. Nakatsuji, J. Chem. Phys. 114, 5117 (2001)
19. C.F. Dion, E.R. Bernstein, J. Chem. Phys. 103, 4907 (1995)
20. M. Tsubouchi, T. Suzuki, J. Phys. Chem. A 107, 10897 (2003)
21. A. Bolovinos, P. Tsikeris, J. Phillips, E. Pantos, G. Andritsopoulos, J. Mol. Spectrosc. 103, 240 (1984)
22. G. Vall-llosera, M. Coreno, P. Erman, M. Huels, K. Jakubowska, A. Kivimäki, E. Rachlew, M. Stankiewicz, Int. J. Mass Spectrom. 275, 55 (2008)
23. T.J. Wasowicz, A. Kivimäki, M. Coreno, M. Zubek, J. Phys. B 47, 055103 (2014)
24. Y.F. Hu et al., Rev. Sci. Instrum. 78, 083109 (2007)
25. T. Reddish, G. Richmond, G. Bagley, J. Wightman, S. Cvejanovic, Rev. Sci. Instrum. 68, 2685 (1997)
26. A.E. Slattery, J.P. Wightman, M.A. MacDonald, S. Cvejanovic, T.J. Reddish, J. Phys. B 33, 483 (2000)
27. M. Śmiałek, E. Szafran, M. MacDonald, L. Zuin, N. Mason, Eur. Phys. J. Special Top. 222, 2361 (2013)
28. M.A. Śmiałek, M. Labuda, J. Guthmuller, M.J. Hubin-Franskin, J. Delwiche, D. Duflot, N.J. Mason, S.V. Hoffmann, N.C. Jones, P. Limao-Vieira, J. Chem. Phys. 141, 104311 (2014)
29. M.A. Śmiałek, M. Labuda, J. Guthmuller, S.V. Hoffmann, N.C. Jones, M.A. MacDonald, L. Zuin, N.J. Mason, P. Limao-Vieira, J. Phys. Chem. A 119, 8647 (2015)
30. K. Huber, C. Jungen, J. Chem. Phys. 92, 850 (1990)
31. D. Shaw, D. Holland, M. MacDonald, A. Hopkirk, M. Hayes, S. McSweeney, Chem. Phys. 166, 379 (1992)
32. K.K. Innes, I.G. Ross, W.R. Moomaw, J. Mol. Spectrosc. 132, 492 (1988)
33. M. Riese, Z. Altug, J. Grottemeyer, Phys. Chem. Chem. Phys. 8, 4441 (2006)
34. S. Tixier, G. Cooper, R. Feng, C. Brion, J. Electron Spectrosc. Relat. Phenom. 123, 185 (2002)

Open Access This is an open access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.