Partial photoionization cross sections of NH_4 and H_3O Rydberg radicals

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Partial photoionization cross sections of NH_4 and H_3O Rydberg radicals

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Photoionization cross sections for various Rydberg series that correspond to ionization channels of ammonium and oxonium Rydberg radicals from the outermost, occupied orbitals of their respective ground states are reported. These properties are known to be relevant in photoelectron dynamics studies. For the present calculations, the molecular-adapted quantum defect orbital method has been employed. A Cooper minimum has been found in the $3sa_1$-kpt_2 Rydberg channel of NH_4 beyond the ionization threshold, which provides the main contribution to the photoionization of this radical. However, no net minimum is found in the partial cross section of H_3O despite the presence of minima in the $3sa_1$-kpe and $3sa_1$-kpa_1 Rydberg channels. The complete oscillator strength distributions spanning the discrete and continuous regions of both radicals exhibit the expected continuity across the ionization threshold. © *2009 American Institute of Physics.* [DOI: 10.1063/1.3168397]

I. INTRODUCTION

Rydberg radicals are transient polyatomic species, which have unstable, dissociative ground states but are stable in excited states. Observations and analysis of the Rydberg emission spectra of H_3 by Herzberg and co-workers[1] sparked interest in the spectroscopy of such molecules. Since then, a number of molecules in specific Rydberg states have been detected as short-lived intermediates in the mechanisms of reactions performed in terrestrial laboratories, as well as in the atmospheres of several planets and in a variety of astronomical objects.[2]

Typical examples of Rydberg radicals are ammonium, NH_4, and oxonium, H_3O. Rydberg states of NH_4 were first observed in 1981 by Herzberg[3] by using hollow-cathode discharges through NH_3. The NH_4^+ ion is present in dense interstellar clouds[4] and has, very recently, been identified in the ion neutral mass spectrometer spectra of Titan obtained by the Cassini spacecraft.[5] The dissociative recombination of electrons with the ammonium cation is a potential source of NH_3 in these environments, with the reaction mechanism being thought to occur via the NH_4 radical. The formation of NH_4 on solid surfaces has also been claimed.[6,7] The H_3O radical was first produced by irradiation of water vapor with ionizing electrons by Melton and Joy.[8] Some authors assert its role as an intermediate in water radiolysis experiments.[9,10] The solvated oxonium radical is a species of major interest in the domain of liquid phase reactivity, for an electron-ion $(H_3O^+ \cdots e^-)_{aq}$ pair it has been found in femtosecond spectroscopy experiments carried out in highly concentrated acidic solution.[11] The H_3O radical also attracted much attention since Andersen *et al.*[12] provided the first evidence that the mechanism of generating the water molecule in interstellar clouds involves dissociative recombination reaction of H_3O^+ with electrons. In this process, electronic states of H_3O

appear as intermediates, as predicted by *ab initio* calculations.[13–17]

Several theoretical and experimental works on the NH_4 and H_3O radicals focused on electronic structure and ground-state stability. In contrast, only a few theoretical works studied Rydberg excited states and transition intensities of NH_4 and H_3O in detail.[17–25] In two recent studies,[26,27] we concentrated our efforts on analyzing the absorption electronic spectrum of NH_4 and H_3O. The study was performed through a combination of *ab initio* electron propagator and coupled cluster methods with the molecular quantum defect orbital (MQDO) formalism. We determined vertical excitation energies, adiabatic ionization potentials, and transition intensities for the bound spectral region of both radicals.

Photoionization processes in NH_4 and H_3O have been less investigated despite the usefulness of photoionization cross section values for estimating the kinetic energy distributions of ejected electrons and fragment ions. Experimental measurements concerning this property are rather difficult to perform, for the lifetimes of both NH_4 and H_3O radicals are short. In this context, Fuke *et al.*[28] studied the photoionization of $NH_4(NH_3)_n$ radicals produced by photolysis of ammonia clusters at 193 nm with one-photon ionization and time-of-flight mass spectroscopy. They determined the ionization potential of NH_4 and also measured the photoionization efficiency curve near the threshold for the isotopic molecule ND_4, a more stable species than NH_4. Following the observations by Fuke *et al.*,[28] theoretical calculations and the resemblance of the ND_4 radical to alkali atoms, Smith and Chupka[29] attributed the unusual behavior of the photoionization cross section in the threshold region to a deep Cooper minimum. The same authors also predicted the existence of such a minimum in the vicinity of the ionization threshold of the NH_4 radical.

In the present study, cross sections for the ionization from the outermost subshell of both species, NH_4 and H_3O, has been analyzed in terms of photoelectron energy. These

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quantities are of key importance in the study of the nature of photoelectrons ejected from matter.[30] An additional goal of this work was to study the possible existence of a Cooper minimum in the partial cross sections leading to the respective cationic cores of the NH_4 and H_3O radicals. A Cooper minimum (defined as a minimum in the cross section) appears as a consequence of a change in sign in the matrix element corresponding to one of the principal channels in the continuum.[30] As Carlson *et al.*[31] indicated, Cooper minima are ideal phenomena for studying photoelectron dynamics. The present results have been obtained with the MQDO method,[32] which was formulated for calculating intensities of transitions involving Rydberg molecular states. The MQDO approach has been broadly used to successfully determine one-photon transition intensities in both the discrete and continuum regions in molecular Rydberg transitions.[33–35]

Finally, the oscillator strength spectral density in the discrete and continuous regions has also been determined for both NH_4 and H_3O. Comparisons of transition probabilities involving the continuum spectral regions of NH_4 and H_3O appear to be unprecedented. One may assess the correctness of the present approach by the criterion of continuity of the differential oscillator strength across the ionization threshold. The present results may also stimulate further inquiry concerning gaps in experimental data or the influence of auto-ionization processes.

II. METHOD OF CALCULATION

The photoionization cross section is a measure of the probability that an absorbed photon will produce ionization and is expressed, in units of megabarns (Mb), as follows:[36]

$$\sigma = 2.6891 \left(\frac{T + k^2}{g_i} \right) |M_{if}|^2, \tag{1}$$

where T is the ionization potential in Rydberg units of the initially bound electron, k^2 is the kinetic energy of the free electron upon ionization, also expressed in Rydberg units, g_i is the degeneracy of the initial state, and M_{if} is the transition matrix element between the initial and final state wave functions, Ψ_i and Ψ_f, respectively. In the electric dipole approximation,

$$M_{if} = \sum_i \sum_f \langle \Psi_i | r | \Psi_f \rangle, \tag{2}$$

where the summation is over all degenerate components in the initial and final states. Ψ_f represents the system consisting of a cationic core plus a free electron. When ionization of outer subshell electrons takes place, the integral in Eq. (2) reduces to an integral over one-electron wave functions, for the cationic core is approximately the same for the initial and final states. These functions should describe the spatial distribution of a single electron before and after the absorption of a photon. The MQDO method provides the one-electron wave functions we employed. This approach, based on a model potential, is appropriate in dealing with molecular Rydberg states because these possess a quasihydrogenic character, with the spherical ionic core replaced by a molecular cation which imposes internal crystal field splitting accord-

ing to its symmetry. A full description of the model is reported in detail in our previous papers.[32,37] Therefore, only the main points will be briefly outlined here.

The radial parts of the MQDO orbitals are the analytical solutions of a one-electron Schrödinger equation involving an effective potential as follows:

$$V(r) = \frac{\lambda(\lambda + 1) - l(l + 1)}{2r^2} - \frac{Z_{net}}{r}, \tag{3}$$

where λ is a parameter which determines the electron screening and Z_{net} is the effective nuclear charge acting on the Rydberg electron. The radial parts of bound-state wave functions are expressed as second Whittaker functions,

$$R(r) = W_{n-\delta, \lambda+1/2}[2Z_{net}r/n - \delta], \tag{4}$$

where δ is the quantum defect which accounts for penetration into the core region.

The corresponding continuum orbitals may be described as first Whittaker functions:

$$R(r) = M_{Z_{net}/ik, \lambda+1/2}(2ikr), \tag{5}$$

and are normalized to a Dirac delta function $\delta(k-k')$. The angular part of the MQDO functions is expressed as a symmetry-adapted linear combination of spherical harmonics such that the molecular orbitals form bases for the irreducible representations of the specific symmetry group of the molecule under study. This allows us to formulate separately the radial and angular contributions to the transition moment, given by Eq. (2), so that the photoionization cross section adopts the following expression:

$$\sigma = 2.6891 \left[\frac{Z_{net}}{(n-\delta)^2} + k^2 \right] \frac{1}{2k} Q\{i \to f\} |R_{if}|^2. \tag{6}$$

$Q\{i \to f\}$ are the angular factors resulting from the integration of the angular functions and the transition operator and R_{if} is the radial transition moment. An important computational advantage of the MQDO model is that the transition integral results in a closed-form analytical expression.

III. RESULTS

The $^2A_1$ ground-state electronic configuration of NH_4 in a tetrahedral, T_d, geometry can be written as $(1a_1)^2(2a_1)^2(1t_2)^6(3a_1)$, while the one for H_3O is $(1a_1)^2(2a_1)^2(1e)^4(3a_1)^2(4a_1)$ in C_{3v} geometry. In both cases, the ground electronic state consists of a very stable closed-shell core and a distant electron in a $3s$ Rydberg orbital.[20] Throughout this work, Rydberg orbitals will be designated as $nl\Gamma_i$, where n and l identify atomic principal and angular momentum quantum numbers and Γ_i is the irreducible representation of the molecular point group.

In the present work, we calculated partial photoionization cross sections (defined as probabilities for one-electron ionization to a particular electronic state of the ion) leading to the ground states of the NH_4^+ and H_3O^+ cores. To do so, we determined the photoionization cross sections for each of the single ionization Rydberg channels, which correspond to excitation of the $3sa_1$ electron in the ground states of the NH_4 and H_3O radicals. A single channel is defined as one in
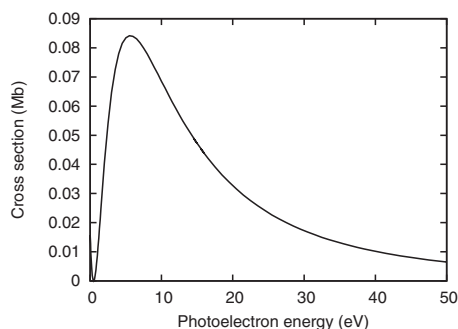
FIG. 1. MQDO photoionization cross sections for the $3sa_1$-kpt_2 Rydberg channel of NH_4 as a function of photoelectron energy.

FIG. 2. MQDO photoionization cross sections for $3sa_1$-kpe and $3sa_1$-kpa_1 Rydberg channels of H_3O and partial photoionization cross section values as a function of photoelectron energy.

which a single electron is excited independently of the others and which leads to an unperturbed Rydberg series with a constant quantum defect.[38] For the ionization of the $3s$ electron in both molecules, the $3s$-kp channel is dominant, for contributions from s and d continuum orbitals vanish according to the $\Delta l = \pm 1$ selection rule for electric dipole transitions. In the case of NH_4, the $3sa_1$-kpt_2 channel represents the main contribution to the partial cross section. However, for the photoionization of H_3O, the splitting of the p orbitals, requires consideration of the $3sa_1$-kpe and $3sa_1$-kpa_1 channels. The ionization potentials used in the present work have been obtained in our previous coupled cluster calculations,[26,27] assuming T_d and a C_{3v} geometries for the ground states of NH_4 and H_3O, respectively. These values are 4.67 eV for NH_4 and 5.50 eV for H_3O. The quantum defects have been obtained through the well known Rydberg formula, using the vertical excitation energies determined in our previous works with the *ab initio* electron propagator formalism.[26,27] For the kpt_2 channel of NH_4, as well as for the kpe and kpa_1 channels of H_3O, we adopted the quantum defects that belong to the orbitals with the lowest n-values of the corresponding Rydberg series, i.e., those of $3pt_2$, $3pe$, and $3pa_1$, respectively. These are expected to be more accurately described than those with higher n. The δ values are equal to 0.842 for the $3pt_2$ orbital of NH_4 and 0.966 and 0.746 for the $3pe$ and $3pa_1$ orbitals of H_3O, respectively.

In Figs. 1 and 2, we plotted the MQDO cross sections for the $3s$-kp channels of the ammonium and the oxonium radicals versus the photoelectron energy, i.e., the photon energy minus the radical's ionization energy. Usually, continuum cross sections behave similarly to those of the hydrogen atom, decreasing monotonically with increasing energy.[38] However, in some atoms, the cross section exhibits a minimum. Such Cooper minima have also been observed in angle-resolved photoelectron spectroscopy using synchrotron radiation for molecules such as Cl_2, HBr, CS_2, COS, and CCl_4.[39–42] As is apparent from Fig. 1, the $3sa_1$-kpt_2 cross section of NH_4 goes to a minimum at a photoelectron energy of about 0.49 eV. This minimum occurs because the kp wave function's nodes contract toward the nucleus (the region of maximum overlap with the ground s-state wave function) as the photoelectron energy increases. As a consequence, the contributions of opposite sign to the matrix element for photoionization balance exactly at a certain value of photoelectron energy, and there will be zero absorption. Above this
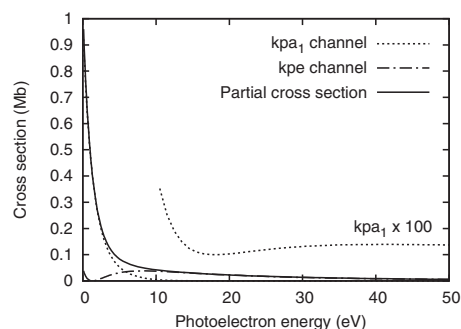
energy, a mismatch between positive and negative contributions to the integral may occur. Therefore, the transition integral increases and passes through a maximum before decreasing again with a trend that begins to approach hydrogenic behavior.
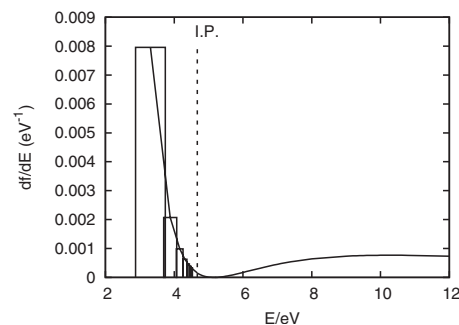
For the H_3O radical, we found a spectral shape similar to those mentioned above for the cross section for the kpe channel, which also falls toward a Cooper minimum near the threshold, at a photoelectron energy of 1.30 eV. For the kpa_1 channel, the cross section diminishes rapidly and monotonically with increasing photoelectron energy until it traverses a minimum at higher photoelectron energy than the one observed for the kpe channel, which occurs about 19.0 eV. This minimum is less pronounced than those found in the kpe channel, for the cross sections are very small in the energy region where they appear. The shift of the Cooper minimum in the kpa_1 channel to larger photoelectron energies may be explained in terms of the quantum defects. According to Gallagher,[43] the energy at which the minimum occurs is a function of the difference between the quantum defects of the ground state and those of the continuum orbitals. Whereas the quantum defect we used in our calculations for the $3sa_1$ Rydberg orbital is 1.43, differences with the kpe and kpa_1 quantum defects are 0.45 and 0.69, respectively. Therefore, in comparison with kpe, kpa_1 penetrates less into the core and its first node appears at a larger distance. Thus, the cancellation between positive and negative contributions to the photoionization matrix element and, hence, the Cooper minimum occurs at higher energies for the kpa_1 channel. Inspection of Fig. 2 reveals that the photoelectron energy region below 5 eV, where the minimum for the kpe Rydberg channel has been detected, is dominated by the kpa_1 cross section and therefore no minimum is found in the partial cross section in this energy range. At higher photoelectron energies, the kpa_1 channel exhibits a Cooper minimum. However, no net minimum has been observed for the partial cross section of the H_3O radical, for the kpe channel is dominant in this region. Unlike their counterparts for the isoelectronic NH_4 case, MQDO calculations on H_3O do not predict a minimum of the partial cross section as a function of photoelectron energy for photoionization leading to the ground state of H_3O^+, although minima have been found in the two single channels. The lower symmetry of the H_3O radical gives rise to two kinds of p-like orbitals, kpa_1 and kpe,

TABLE I. Partial cross sections, in units of Mb, for the photoionization of NH_4 and H_3O leading to the ground state of the cationic cores.

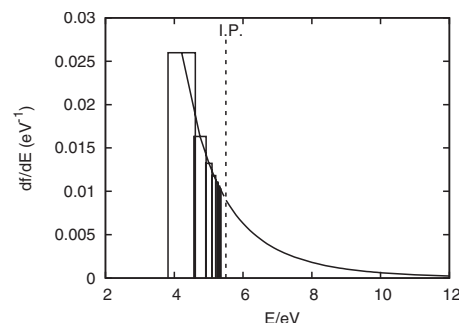| Photoelectron energy (eV)	NH_4	H_3O
0.01	0.0157	1.0315
0.05	0.0128	0.9987
0.1	0.0096	0.9597
0.2	0.0049	0.8870
0.3	0.0019	0.8210
0.4	0.0004	0.7609
0.5	0.0000	0.7061
0.6	0.0006	0.6562
0.7	0.0018	0.6106
0.8	0.0037	0.5689
0.9	0.0060	0.5308
1.0	0.0087	0.4958
1.1	0.0116	0.4638
1.2	0.0147	0.4343
1.3	0.0179	0.4073
1.4	0.0212	0.3824
1.5	0.0245	0.3594
2.5	0.0541	0.1233
4.5	0.0815	0.0697
6.5	0.0831	0.0528
8.5	0.0756	0.0446
10.5	0.0661	0.0391
12.5	0.0570	0.0346
14.5	0.0490	0.0308
16.5	0.0421	0.0275
18.5	0.0364	0.0246
19.5	0.0339	0.0233
20.5	0.0316	0.0220
22.5	0.0275	0.0198
24.5	0.0242	0.0179
26.5	0.0213	0.0162
28.5	0.0188	0.0147
30.5	0.0168	0.0133
32.5	0.0150	0.0122
34.5	0.0134	0.0111
36.5	0.0121	0.0102
38.5	0.0109	0.0094
40.5	0.0099	0.0086
42.5	0.0090	0.0080
44.5	0.0082	0.0074
46.5	0.0075	0.0068
48.5	0.0069	0.0064
50.5	0.0063	0.0059

FIG. 3. MQDO oscillator strength spectral density for bound and continuum spectral regions of the $3sa_1$-npt_2 ($n=4-10$, continuum) Rydberg series in NH_4 as a function of photon energy.

the present study, we found a minimum in the continuum region of the spectrum. Because of their reliance on ND_4 photoionization efficiency measurements, Smith and Chupka did not consider their estimate of the location of the Cooper minimum to be reliable.[29]

The discrete regions of the NH_4 and H_3O spectra provide additional insight into the location of Cooper minima. Figures 3–5 exhibit the oscillator strength spectral density, df/dE, as a function of incident photon energy in the discrete and continuum spectral regions for each of the individual p Rydberg channels of NH_4 and H_3O. These results are based on the procedure developed by Fano and Cooper.[44] Above the ionization limit, df/dE is related to the cross section through the following equation:

$$\sigma(E) = 1.098 \times 10^{-16}\ \text{cm}^2\ \text{eV}\left(\frac{df}{dE}\right). \tag{7}$$

Below the ionization limit, the oscillator strength, or f-value, is plotted as a set of rectangular blocks whose area is equal to the f-value for the "n" transition. The base of each block has a width equal to $2R/n^{*3}$, where R is the Rydberg constant, and its height is equal to fdn^*/dE_n. Each of the blocks is centered at the energy of the upper state of the transition, E_n. The f-values used in this procedure have been taken from our previous works on the H_3O and NH_4 radicals,[26,27] which were also obtained from MQDO calculations. In the case of NH_4, we reported emission coefficients, A_{fi}, which have been now converted to f-values using the well known expression,

whereas in NH_4 all p-like orbitals are degenerate. Despite the isoelectronic relationship between NH_4 and OH_3, the lack of threefold degeneracy in the latter radical leads to two final symmetry channels with distinct cross-section curves. Therefore, no Cooper minimum in the total cross section is observed. Numerical values for the partial photoionization cross sections of both radicals are collected in Table I.

The possible existence of a Cooper minimum in NH_4 was studied in the theoretical work of Smith and Chupka.[29] These authors postulated the occurrence of a Cooper minimum in this radical on the basis of observations in the photoionization of ND_4 carried out by Fuke *et al.*[28] Whereas they predicted a minimum just below the ionization threshold, in

FIG. 4. MQDO oscillator strength spectral density for bound and continuum spectral regions of the $3sa_1$-npa_1 ($n=4-10$, continuum) Rydberg series in H_3O as a function of photon energy.
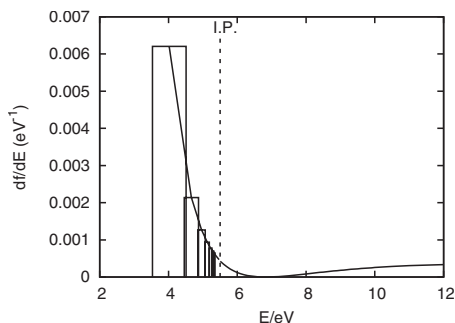
FIG. 5. MQDO oscillator strength spectral density for bound and continuum spectral regions of the $3sa_1$-npe ($n=4-10$, continuum) Rydberg series in H_3O as a function of photon energy.

$$A_{fi} = 6.6702 \times 10^{15} \lambda^2 (g_i/g_f) f_{if}, \qquad (8)$$

where g_i and g_f are the statistical weights of the initial and final states in the absorption process, respectively, the wavelength λ is expressed in angstroms and A_{if} is expressed in s^{-1}. Because the corresponding values for excited states with $n=3$ are greater in magnitude than the others, these values have not been included in the graphs.

An inspection of Figs. 3–5 reveals that no minima are present in the values of the oscillator strength spectral density in the bound spectral region for the Rydberg channels of both radicals. This result, along with the present MQDO cross sections, suggests that the Cooper minimum for NH_4 occurs just above the ionization threshold and not below, as proposed by Smith and Chupka.[29] Moreover, for both radicals, complete consistency between the presently calculated photoionization cross sections and our previous results on oscillator strengths is obtained such that the oscillator strength spectral density passes smoothly from the bound to the continuum. These features, as well as the close agreement between our previous f-values and data available in the literature, confirm the reliability of the present MQDO cross sections. Our previously reported results for H_3O were consistent with the most recent and accurate *ab initio* calculations by Luo and Jungen.[17] In the case of NH_4, our calculations were in good agreement with other theoretical data obtained with a self-consisted field method using floating spherical Slater orbital basis functions[20] and second-order Rayleigh–Schrödinger perturbation theory.[19]

Continuity of the oscillator strength spectral density near the ionization energy is a fundamental property, which derives from the continuity of wave functions across the ionization threshold.[37] With this advantage, one can interpolate the value of the cross section at the ionization threshold, a quantity that is not possible to determine by ordinary calculations, given that $n \rightarrow \infty$. In the present work, an interpolated value for the cross section at the threshold may be inferred from the graphs. The MQDO partial cross sections at the first ionization limit are 0.02 Mb for NH_4 and 1.04 Mb for H_3O. The latter has been obtained by the addition of the values corresponding to each of the single Rydberg channels, 0.99 and 0.05 Mb, for kpa_1 and kpe, respectively.

Comparison with Na and K alkali atoms provides an additional test of the location of our minimum cross section of NH_4. Herzberg suggested the existence of significant re-
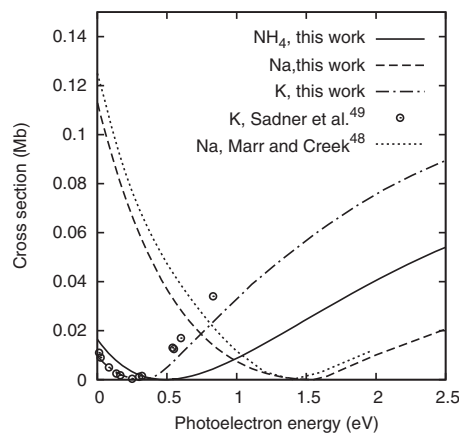

FIG. 6. Photoionization cross sections of NH_4, Na I, and K I as a function of photoelectron energy.

semblances between the Rydberg spectrum of a molecule and that of its united atom limit.[45] On the other hand, Mulliken[46] claimed that the chemistry of NH_4 should resemble that of potassium rather than that of isoelectronic sodium. Thus, similar behavior would be expected in the partial cross sections of NH_4 and those of Na and K alkali atoms. Photoionization cross sections from the outermost electrons of Na and K atoms in the vicinity of their minima also have been calculated in this study with the aid of tabulated ionization potentials and electronic energies.[47] In Fig. 6, the current calculated cross sections of Na and K, together with the MQDO results on the NH_4, have been plotted versus photoelectron energy in the threshold region. To test the quality of our methodology, we also included reliable experimental data found in the literature for the alkali atoms Na and K. Marr and Creek reported photoionization curves for the Na atom.[48] In the case of K, we represented the most recent measurements by Sandner *et al.*[49] using a pulsed laser followed by time-of-flight analysis. Our atomic cross sections agree very well with the experimental values in Fig. 6. Such agreement confirms the reliability of our results and the adequacy of our methodology in dealing with these kinds of systems. Moreover, the cross sections for the molecular radical are nearer to those of the K atom than those of Na. In Table II, we collected the present theoretical cross-section values at the

TABLE II. Cross sections at the threshold, in Mb, and minimum cross section location, expressed as photoelectron energy in eV.

	NH_4[a]	Na I	K I
$\sigma_{threshold}$/Mb	0.02	0.116[a]	0.009[a]
		0.125[b]	0.007[b]
		0.130[c]	0.011[d]
			0.010–0.012[e]
$\varepsilon_{minimum}$/eV	0.49	1.45[a]	0.29[a]
		1.31[b]	0.20[b]
		1.06–1.39[c]	0.24[d]
			0.18–0.43[e]

[a]This work.
[b]Marr and Creek (Ref. 48).
[c]Hudson and Carter (Ref. 50).
[d]Sandnet *et al.* (Ref. 49).
[e]Hudson and Carter (Ref. 51).

threshold and the photoelectron energy at which the Cooper minimum occurs for the NH$_4$ radical and for the alkali atoms. The experimental data for Na and K atoms have also been included. Inspection of Table II reveals again the existence of important analogies among the photoionization spectra of NH$_4$ and the K atom, not only in the location of the Cooper minimum, but also in the value for the cross section at the first ionization limit. These facts support the earlier prediction by Mulliken regarding the closer analogy between the ammonium radical and the K atom than with its isoelectronic atom, Na. The cross section of NH$_4$ mimics the behavior of the united atom, Na, with regard to the existence of a Cooper minimum above the ionization threshold.

IV. CONCLUSIONS

Partial photoionization cross sections of the Rydberg radicals of NH$_4$ and H$_3$O have been obtained. A thorough analysis of the oscillator strength distribution in the discrete and continuum spectral regions of both species in terms of photon energy has also been carried out. A Cooper minimum has been found for the photoionization leading to the ground state of the cationic core for NH$_4$, but not for H$_3$O. This kind of phenomenon may be useful in the analysis of the nature of continuum orbitals of both radicals and, thus, in the study of their photoelectron dynamics. In addition, we hope these properties may shed some light on the important processes in which these molecules could be involved.

ACKNOWLEDGMENTS

[1] G. Herzberg, J. Chem. Phys. **70**, 4806 (1979); I. Dabrowski and G. Herzberg, Can. J. Phys. **58**, 1238 (1980); G. Herzberg and J. K. G. Watson, *ibid.* **58**, 1250 (1980); G. Herzberg, H. Lew, J. Sloan, and J. K. G. Watson, *ibid.* **59**, 428 (1981); G. Herzberg, J. T. Hougen, and J. K. G. Watson, *ibid.* **60**, 1261 (1982).
[2] M. E. Jacox, J. Phys. Chem. Ref. Data Monogr **3**, 1 (1994).
[3] G. Herzberg, Faraday Discuss. Chem. Soc. **71**, 165 (1981).
[4] A. Sternberg and A. Dalgarno, Astrophys. J., Suppl. Ser. **99**, 565 (1995).
[5] V. Vuitton, R. V. Yelle, and V. G. Anicich, Astrophys. J. **647**, L175 (2006).
[6] C. E. Melton, J. Am. Chem. Soc. **84**, 1491 (1962).
[7] C. E. Melton, J. Chem. Phys. **45**, 4414 (1966).
[8] C. E. Melton and H. W. Joy, J. Chem. Phys. **46**, 4275 (1967).
[9] J. L. Magee, Radiat. Res. Suppl. **4**, 20 (1964).
[10] T. J. Sworski, J. Am. Chem. Soc. **86**, 5034 (1964).
[11] Y. Gauduel, S. Pommeret, and A. Antonetti, J. Phys. Chem. **97**, 134 (1993); Y. Gaudel, in *Ultrafast Reaction Dynamics and Solvent Effects*, edited by Y. Gaudel and P. J. Rossky (AIP, New York, 1994), Vol. 298, pp 191–204.
[12] L. H. Andersen, O. Heber, D. Kella, H. B. Pedersen, L. Vejby-Christensen, and D. Zajfman, Phys. Rev. Lett. **77**, 4891 (1996).
[13] J. K. Park, Chem. Phys. Lett. **315**, 119 (1999).
[14] J. K. Park, B. G. Kim, and I. S. Koo, Chem. Phys. Lett. **356**, 63 (2002).
[15] A. E. Ketvirtis and J. Simons, J. Phys. Chem. A **103**, 6552 (1999).
[16] M. Kayanuma, T. Taketsugu, and K. Ishii, Chem. Phys. Lett. **418**, 511 (2006).
[17] M. Luo and M. Jungen, Chem. Phys. **241**, 297 (1999).
[18] S. Havriliak and H. F. King, J. Am. Chem. Soc. **105**, 4 (1983).
[19] S. Havriliak, T. R. Furlani, and H. F. King, Can. J. Phys. **62**, 1336 (1984).
[20] S. Raynor and D. Herschbach, J. Phys. Chem. **86**, 3592 (1982).
[21] B. N. McMaster, J. Mrozek, and V. H. Smith, Chem. Phys. **73**, 131 (1982).
[22] J. Kaspar and V. H. Jr Smith, Chem. Phys. **90**, 47 (1984).
[23] G. R. Wight and C. E. Brion, Chem. Phys. Lett. **26**, 607 (1974).
[24] E. Kassab and E. Evleth, J. Am. Chem. Soc. **109**, 1653 (1987).
[25] G. R. Broclawik, J. Mrozek, and V. H. Jr Smith, Chem. Phys. **66**, 417 (1982).
[26] J. V. Ortiz, I. Martín, A. M. Velasco, and C. Lavín, J. Chem. Phys. **120**, 7949 (2004).
[27] J. Melin, J. V. Ortiz, I. Martín, A. M. Velasco, and C. Lavín, J. Chem. Phys. **122**, 234317 (2005).
[28] K. Fuke, R. Takasu, and F. Misaizu, Chem. Phys. Lett. **229**, 597 (1994).
[29] J. M. Smith and W. A. Chupka, Chem. Phys. Lett. **250**, 589 (1996).
[30] J. W. Cooper, Phys. Rev. **128**, 681 (1962).
[31] T. A. Carlson, M. O. Krause, W. A. Svensson, P. Gerard, F. A. Grimm, T. A. Whithley, B. P. Pullen, Z. Phys D: At., Mol. Clusters **2**, 309 (1986).
[32] I. Martín, C. Lavín, A. M. Velasco, M. O. Martín, J. Karwowski, and G. H. F. Diercksen, Chem. Phys. **202**, 307 (1996).
[33] A. M. Velasco, I. Martín, and C. Lavín, Chem. Phys. Lett. **264**, 579 (1997).
[34] E. Bustos, A. M. Velasco, I. Martín, and C. Lavín, J. Phys. Chem. A **106**, 35 (2002).
[35] C. Lavín, A. M. Velasco, and I. Martín, Astrophys. J. **644**, 1334 (2006).
[36] G. V. Marr, *Photoionization Processes in Gases* (Academic, New York, 1967).
[37] I. Martín and G. Simons, J. Chem. Phys. **62**, 4799 (1975).
[38] J.-P. Connerade, *Highly Excited Atoms* (Cambridge University Press, Cambridge, 1998).
[39] T. A. Carlson, M. O. Krause, F. A. Grimm, P. Keller, and J. W. Taylor, J. Chem. Phys. **77**, 5340 (1982).
[40] T. A. Carlson, M. O. Krause, and F. A. Grimm, J. Chem. Phys. **77**, 1701 (1982).
[41] T. A. Carlson, A. Fahlman, M. O. Krause, T. A. Whitley, and F. A. Grimm, J. Chem. Phys. **81**, 5389 (1984).
[42] T. A. Carlson, M. O. Krause, F. A. Grimm, and T. A. Whitley, J. Chem. Phys. **78**, 638 (1983).
[43] T. F. Gallagher, *Rydberg Atoms* (Cambridge University Press, Cambridge, 1994).
[44] U. Fano and J. W. Cooper, Rev. Mod. Phys. **40**, 441 (1968).
[45] G. Herzberg, Annu. Rev. Phys. Chem. **38**, 27 (1987).
[46] R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933).
[47] NIST Atomic Spectra Database, version3.1.5, http://physics.nist.gov/asd3, National Institute of Standards and Technology, Gaithersburg, MD.
[48] G. V. Marr and D. M. Creek, Proc. R. Soc. London, Ser. A **304**, 233 (1968).
[49] W. Sandner, T. f. Gallaguer, K. A. Safinya, and F. Gounand, Phys. Rev. A **23**, 2732 (1981).
[50] R. D. Hudson and V. L. Carter, J. Opt. Soc. Am. **57**, 651 (1967).
[51] R. D. Hudson and V. L. Carter, Phys. Rev. **139**, A1426 (1965).