Multireference calculation of lifetime of $A^2\Pi_u$ state in nitrogen-molecule cation*

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This paper utilizes multireference configuration interaction theory to calculate the lifetime of $A^2\Pi_u$ state for nitrogen molecular ion N_2^+. It obtains the transition moment function for $A^2\Pi_u \rightarrow X^2\Sigma_g^+$, Franck–Condon factors between vibrational levels of the two states. The calculated lifetimes are 16.81, 14.62, 13.10, 12.18, 11.40, and 11.64 μs for $v' = 0$, 1, 2, 3, 4, 5 vibrational levels of $A^2\Pi_u$ state, respectively, which are in excellent agreement with available experimental values.

Keywords: lifetime, Franck–Condon factor, nitrogen molecular ion
PACC: 3370F, 3120T, 3420B, 3370C

1. Introduction

The study of a singly charged nitrogen molecular ion N_2^+ arises from astrophysical interest, and the ground state of N_2^+ was ever the topic of theorists.[1−3] The ground state of N_2^+ is $X^2\Sigma_g^+$ as determined theoretically by Verhaegen *et al.* and the $A^2\Pi_u$ state lies 1.17 eV above the ground state.[3] Since nitrogen is abundant in the atmosphere, many theoretical and experimental studies for the N_2 spectra were reported.[4,5] As the rapid development of synchrotron radiation and its use in molecular physics,[6,7] the photoionization and inner shell excitation of the molecule have become the hotspots. The photoionization of nitrogen molecule, the emission spectra[8,9] and the excited states[10,11] of doubly charged nitrogen N_2^{2+} were investigated by the photoion–photoion coincidence method experimentally and multireference configuration interaction (MRCI) method theoretically.

The $N_2^+(A^2\Pi_u)$ plays an vital role in the aurora and disturbed the upper atmosphere. The Meinel bands ($A^2\Pi_u \rightarrow X^2\Sigma_g^+$) are bright features in the aurora and afterglow. In previous reports, the electron-impact excitation of Meinel bands,[12] $^2\Pi_g \rightarrow A^2\Pi_u$ transition in N_2^+,[13] and the lifetime of $A^2\Pi_u$ state[14] were studied experimentally. But few *ab initio* works were found to report the Meinel bands and the lifetime of $A^2\Pi_u$ for N_2^+.

The present work adopted MRCI method for the potential energy curves(PECs) of $X^2\Sigma_g^+$, $A^2\Pi_u$ states, and the electronic dipole moments for $A^2\Pi_u \rightarrow X^2\Sigma_g^+$ transitions were calculated at same level of theory. The Franck–Condon (FC) factors(FCFs) between vibrational level v' of upper electronic state and vibrational manifold v'' of lower electronic state were obtained based on the fitting PECs. The spontaneous radiative Einstein coefficients $A_{v'v''}$ for $A^2\Pi_u(v') \rightarrow X^2\Sigma_g^+(v'')$ were calculated, and the natural lifetimes for $A^2\Pi_u(v' = 0, 1, 2, 3, 4, 5)$ were obtained.

2. Computational methods

The electronic structure calculations were performed by internal contraction MRCI[15] method using Molpro2006.1 package.[16] The Dunning's correlation-consistent cc-pVQZ basis set[17] was used in this work. The active space consists of $2s\sigma_g$, $2s\sigma_u$, $2p\sigma_g$, $2p\pi_u$, $2p\pi_g$, $2p\sigma_u$ orbitals, and the 1 s core orbitals were excluded in the correlation calculations.

The lifetime $\tau_{v'}$ is the inverse of sum of the Einstein coefficients $A_{v'v''}$ over v'', that is

$$\tau_{v'} = \left(\sum_{v''} A_{v'v''} \right)^{-1}. \quad (1)$$

3. Results and discussion

3.1. The PECs of N_2^+

The PECs of N_2^+ were constructed from 48 single state MRCI calculations at internuclear distances

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from 0.09 nm to 0.4 nm for $X^2\Sigma_g^+$, $A^2\Pi_u$ states. Considering the size consistency, we used the Davidson correction,[16] denoted as MRCI+Q for MRCI results. The spectroscopic constants are fitted based on the calculated MRCI+Q PECs and listed in Table 1. The calculated equilibrium bond distances r_e for ground state $X^2\Sigma_g^+$ and $A^2\Pi_u$ state differ from the experimental results within 3×10^{-4} nm error. The calculated spectroscopic constants ω_e are 2193.3 and 1890.0cm^{-1} for $X^2\Sigma_g^+$ and $A^2\Pi_u$ state, the latter is in good agreement with experimental value 1902.82 cm^{-1}. The anharmonic constant $\omega_e x_e$ for $A^2\Pi_u$ state is also consistent with experiment within 1 cm^{-1}. The relative energy difference between $A^2\Pi_u$ and $X^2\Sigma_g^+$ state is 8927 cm^{-1} in present work, which is in accordance with early *ab initio* result by Verhaegen *et al.*[3] with 0.06 eV error.

Table 1. Spectroscopic constants in cm^{-1} for X $^2\Sigma_g^+$ and $A^2\Pi_u$ state of N_2^+.

state	r_e/nm	ω_e	$\omega_e x_e$	T_e
X $^2\Sigma_g^+$	0.11204	2193.3	16.9	0
	0.1118[a]			
$A^2\Pi_u$	0.11789	1890.0	15.0	8927
	0.1176[a]	1902.82[b]	14.92[b]	

[a] Experimental values collected from Ref. [3].

[b] Revised experimental values in Ref. [13].

3.2. The lifetime of $A^2\Pi_u$ state

The calculated PECs of $A^2\Pi_u$ state and $X^2\Sigma_g^+$ state at MRCI+Q/cc-pvQz level of theory, along with the transition moment of $A^2\Pi_u \rightarrow X^2\Sigma_g^+$, are presented in Fig. 1. The transition moment was fitted to quartic polynomial function in 0.09–0.20 nm, and was found to be in linear in FC region with an average value ∼0.25 atomic units, which agrees with Popkie and co-worker's early experiment.[18]

The FCFs and $v' \rightarrow v''$ transition energies are required to compute the spontaneous radiative coefficients $A_{v'v''}$ for sub-transition $v' \rightarrow v''$ in $A^2\Pi_u \rightarrow X^2\Sigma_g^+$ process. To get accurate transition energies, a larger basis set cc-pv5z was used in MRCI+Q calculation for $A_{v'v''}$. The FCFs for $v' \rightarrow v''$, which are dominant in $A_{v'v''}$, are shown in Table 2. The radiative coefficients $A_{v'v''}$ and the lifetime of $A^2\Pi_u(v' = 0-5)$ are presented in Table 3. The radiative lifetime is dominant by one or two $v' \rightarrow v''$ sub-transition process, for example, the 1-0 and 1-2 sub-transitions are dominant in the lifetime of $A^2\Pi_u(v' = 1)$. The calculated natural lifetimes are 16.81, 14.62, 13.10, 12.18, 11.40, and 11.64 μs for $v' = 0-5$ of $A^2\Pi_u$ state, respectively. The measured lifetimes[14] for $v' = 3$, 4, 5 are 12.23±0.19, 11.42±0.19, and 12.2±0.9 μs, respectively. The calculated lifetimes in present work are within the error bars in agreement with the experimental values by Hollstein *et al.*[14] In conclusion, the present level of theory was tested as an efficient method in the natural lifetime calculation.

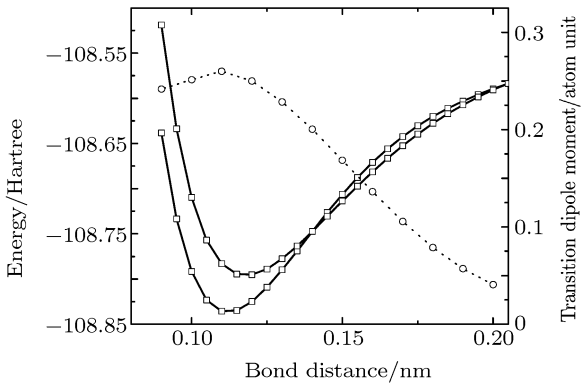


Fig. 1. The PECs for $A^2\Pi_u$ and $X^2\Sigma_g^+$ state (left and bottom axis) along with the A–X transition moment in atomic units (right and top axis).

Table 2. Franck–Condon factors of $A^2\Pi_u(v')$-$X^2\Sigma_g^+(v'')$.

v''	v'					
	0	1	2	3	4	5
0	0.4811	0.3240	0.1334	0.0440	0.0128	0.0035
1	0.3775	0.0344	0.2279	0.1979	0.1014	0.0405
2	0.1197	0.3394	0.0192	0.0832	0.1755	0.1382
3	0.0198	0.2337	0.1909	0.1020	0.0083	0.1096
4	0.0018	0.0605	0.2938	0.0670	0.1544	0.0061

Table 3. The radiative coefficients $A_{v'v''}$ and the lifetime of $A^2\Pi_u(v' = 0 - 5)$.

$10^3 \times A_{v'v''}/s^{-1}$						
v''	v'					
	0	1	2	3	4	5
0	43.400	51.621	33.963	16.506	6.792	2.483
1	14.603	2.772	32.800	45.424	34.760	19.462
2	1.448	11.516	1.381	10.706	36.548	42.873
3	0.036	2.390	5.660	6.475	0.960	20.498
4	$< 10^{-5}$	0.085	2.523	1.716	8.695	0.627
lifetime τ/μs	16.81	14.62	13.10	12.18 12.23±0.19[a]	11.40 11.42±0.19[a]	11.64 12.2±0.9[a]

[a] Experimental values from Ref. [14].

4. Summary

The radiative lifetimes for $A^2\Pi_u(v' = 0, 1, 2, 3, 4, 5)$ state of N_2^+ were calculated based on *ab initio* results by the MRCI method using cc-pvQ(5)z basis set. The calculated values are in good accordance with the experiment. The present level of theory was tested to be an effective method for transition properties of small molecules and ions.

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