The Journal of Chemical Physics ARTICLE pubs.aip.org/aip/jcp

Electronic states of the N_2^+ ion dissociating to the four lowest dissociation limits: Energies, transition dipole moments, and Einstein coefficients

Cite as: J. Chem. Phys. **161**, 244306 (2025); doi: 10.1063/5.0245622
Submitted: 28 October 2024 • Accepted: 4 December 2024 •
Published Online: 30 December 2024

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ABSTRACT

This study presents Born–Oppenheimer energies and transition dipole moments of the 36 lowest electronic states of the N_2^+ ion as a function of internuclear distance in the interval between 1.5 and 10 bohrs obtained in first-principles calculations. The electronic states are of the total electronic spin $S = 1/2, 3/2$, and $5/2$, dissociating toward to the lowest four $N(^4S^0) + N^+(^3P)$, $N(^2P^0) + N^+(^3P)$, $N(^2D^0) + N^+(^3P)$, and $N(^4S^0) + N^+(^1D)$ dissociation limits. Energies of the lowest states, dissociating toward to the $N(^4S^0) + N^+(^3P)$ limit, are computed accounting for relativistic corrections. The obtained potential energy curves and the transition dipole moments are employed to compute vibrational energies in these states, vibronic transition dipole moments, and the Einstein coefficients for radiative transitions between the vibronic levels.

I. INTRODUCTION

The nitrogen molecule N_2 and its molecular cation N_2^+ play an important role in several fields of physics and chemistry, such as in combustion or air plasma, formed, for example, during spacecraft re-entry, by electric discharge, or by a strong laser field. For these reasons, the two species have been extensively studied in theory and experiment. For interpretation of experiments and modeling the N_2/N_2^+ plasma behavior under extreme conditions, where an experimental approach is expensive or impossible, availability of molecular data obtained theoretically, is crucial. Typically, the required data include energies of several electronic Born–Oppenheimer states of the molecules, rotational and vibrational energies, transition dipole moments between the electronic and vibronic levels, cross sections for photoionization of N_2 and for various processes occurring in electron-N_2^+ collisions, and also cross sections and rate coefficients for processes occurring in collisions of N_2/N_2^+ with other atoms and molecules. In some situations, rotationally resolved data might also be of interest for low-temperature plasma; however, for the N_2^+ plasma, the density of rotational states is high so that the rotational motion could be treated classically or neglected.

There have been many studies determining the lowest Born–Oppenheimer potential energies curves (PECs) of N_2^+ since the study by Nesbet[1] in 1965. A good review of the previous theoretical calculations is given by Liu *et al.*[2] The study[2] itself provided the PECs for 25 lowest electronic states, computed with the internally contracted MRCI (multi-reference configuration interaction) method, accounting for the Davidson correction and using the cc-pV5Z basis set and extrapolated to the complete basis set. In that study, PECs accounting for the spin–orbit coupling were also reported. A later study by Ferchichi *et al.*[3] has provided very accurate PECs for the ground state $X^2\Sigma_g^+$ and one of the excited doublet states, $B^2\Sigma_u^+$. Energies of vibrational states obtained with the PECs are in excellent agreement with the experiment. Although the PECs of N_2^+ are available in the literature—in particular, Liu *et al.*[2] have provided numerical data for the PECs of the 25 states—the electronic dipole moments have been determined previously only for a few transitions—to our knowledge, only between the $X^2\Sigma_g^+$ and $B^2\Sigma_u^+$

states,[3,4] between the $X^2\Sigma_g^+$ and $C^2\Sigma_u^+$ states,[4] and between the $X^2\Sigma_g^+$ and $C^2\Sigma_u^+$ states.[4] For accurate modeling of interaction of nitrogen plasma with radiation, involving several lowest electronic states of N_2^+, dipole moments for several other transitions are needed. In this study, we have computed the 36 PECs correlating at large internuclear distances with the $N(^4S^0) + N^+(^3P)$, $N(^2P^0) + N^+(^3P)$, $N(^2D^0) + N^+(^3P)$, and $N(^4S^0) + N^+(^1D)$ dissociation limits, having the total electronic spin $S = 1/2, 3/2, 5/2$. The second objective of the study is the determination of the dipole moments between several lowest electronic states and between vibrational levels in their states.

The rest of this article is organized in the following way: In Sec. II, we discuss the performed *ab initio* calculations and present obtained PECs. Computed transition dipole moments between electronic states are considered in Sec. III, while Sec. IV is devoted to the vibronic transitions and Einstein coefficients. Section V concludes this work.

II. POTENTIAL ENERGY CURVES

To obtain fixed-nuclei electronic energies and transition dipole moments for N_2^+, the Molpro suite of codes[5] is used. The aug-cc-pv5z (AV5Z) basis set was used to obtain the Hartree–Fock orbitals. The orbitals were then optimized using the MCSCF (multi-configuration self-consistent field) method. The obtained natural orbitals were used in the following MRCI (multi-reference configuration interaction) calculations. In the calculations, two lowest orbitals, a_g and one b_{1u}, representing the 1*s* atomic orbitals of each atom, were treated as closed. The remaining 9 electrons were distributed over 12 actives orbitals, $2a_g$, $2b_{3u}$, $2b_{2u}$, $2b_{1u}$, $2b_{2g}$, and $2b_{3g}$. For a better precision of the PECs of the lowest states, converging to the lowest dissociation limit, relativistic calculations have also performed using the MRCI-F12b method and the aug-cc-pCVQZ-F12 basis set,[5] including the 8th-order correction of the Dirac Hamiltonian and a second-order correction of the Pauli Hamiltonian. The active space used in these calculations was made of 8 orbitals, $2a_g$, $1b_{3u}$, $1b_{2u}$, $2b_{1u}$, $1b_{2g}$, and $1b_{3g}$. The combination of the chosen basis set and method allowed us to account for all electron correlations and the relativistic corrections.

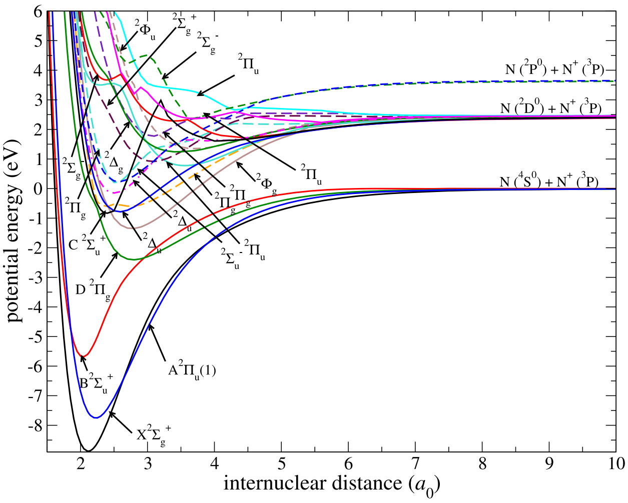

FIG. 1. Potential energy curves of the doublet electronic states.

The calculations were performed for 60 internuclear distances R between 1.4 and 10 bohrs. The potential energy curves for the

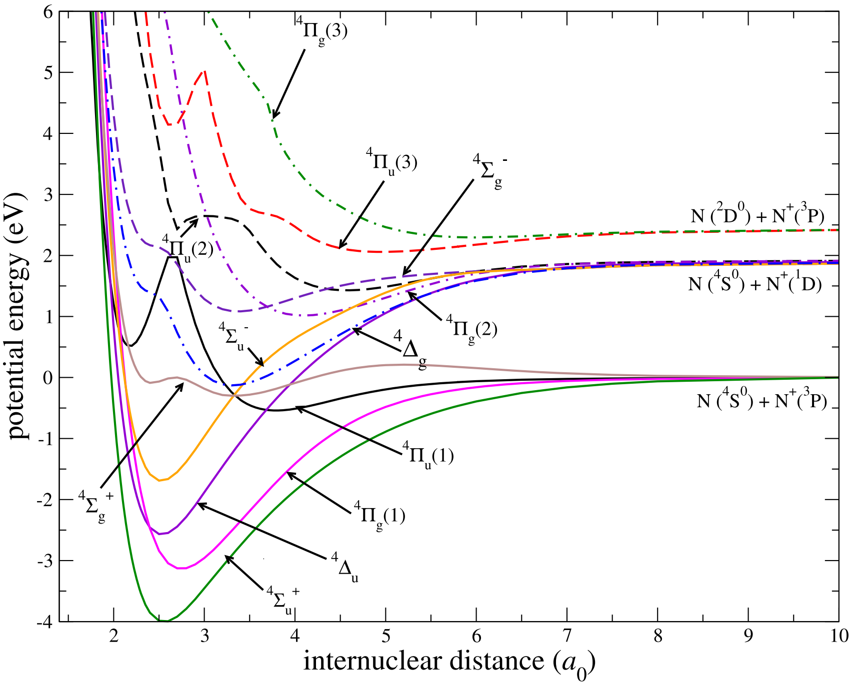

FIG. 2. Potential energy curves of the quartet electronic states.

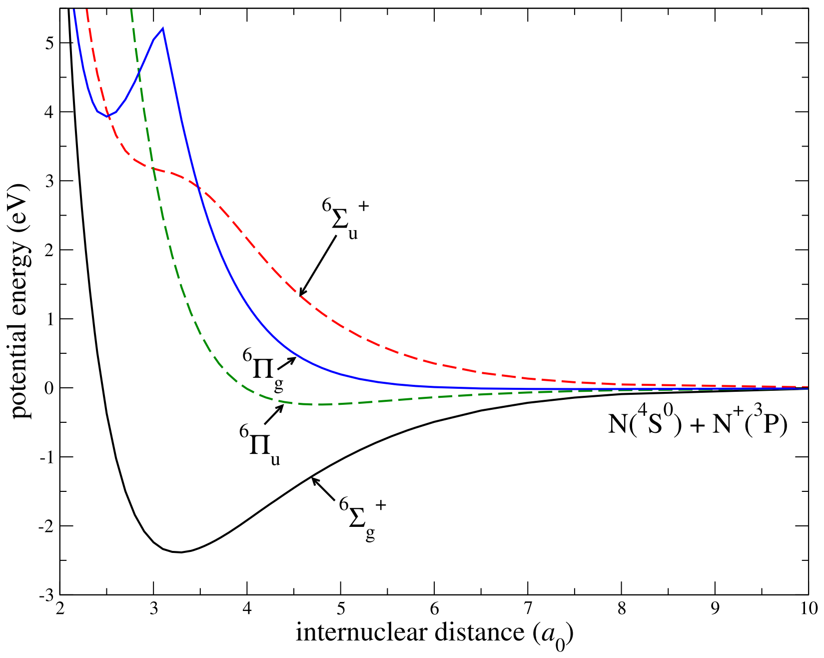

FIG. 3. Potential energy curves (PEC) of the sextet electronic states.

20 doublet, 12 quartet, and 4 sextet electronic states were computed. The set covers all electronic states converging to the four lowest dissociation limits N(^{4}S^0) + N$^+$(^{3}P), N(^{2}P^0) + N$^+$(^{3}P), N(^{2}D^0) + N$^+$(^{3}P), and N(^{4}S^0) + N$^+$(^{1}D). The potential curves, computed without the relativistic correction, are shown in Figs. 1–3. The PECs of certain excited states, such as C$^2\Sigma_u^+$ at 3.2 bohrs (see Fig. 1) are not smooth due to sudden avoided crossings with PECs attached to higher dissociation limit, not computed in this study.

Figure 4 shows all PECs converging to the N(^{4}S^0) + N$^+$(^{3}P) and computed accounting for relativistic corrections as discussed above.

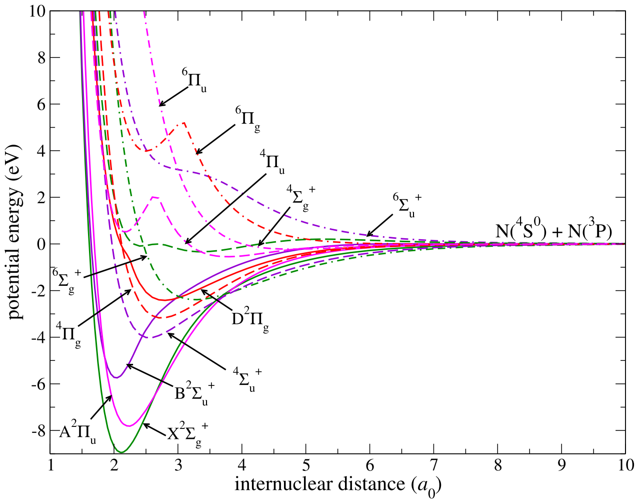

FIG. 4. Summary of the PECs converging to the first dissociation limit, N(^{4}S^0) + N$^+$(^{3}P). The curves, shown in the figure, are obtained accounting for relativistic corrections.

TABLE I. N_2^+ dissociation energies (in eV), obtained in the present study and compared to the data from the previous calculations by Liu *et al.*[2] and from the NIST database.[6]

Dissociation limit	Present	Prev. calc.[2]	Experiment[6]	Molecular states
N(^{4} S^0) + N$^+$(^{3}P)	0.0	0.0	0.0	$^2\Sigma_g^+$, $^4\Sigma_g^+$, $^6\Sigma_g^+$ $^2\Sigma_u^+$, $^4\Sigma_u^+$, $^6\Sigma_u^+$ $^2\Pi_u$, $^4\Pi_u$, $^6\Pi_u$ $^2\Pi_g$, $^4\Pi_g$, $^6\Pi_g$
N(^{4}S^0) + N$^+$(^{1}D)	1.898	1.889	1.898	$^4\Sigma_g^+$, $^4\Sigma_u^+$ $^4\Pi_g$, $^4\Pi_u$ $^4\Delta_g$, $^4\Delta_u$ $^4\Sigma_g^-$, $^4\Sigma_u^-$
N(^{2}D^0) + N$^+$(^{3}P)	2.389	2.389	2.384	$^2\Sigma_g^+$, $^4\Sigma_g^+$ $^2\Sigma_u^+$, $^4\Sigma_g^+$ $^2\Pi_u$, $^4\Pi_u$ $^2\Pi_g$, $^4\Pi_g$ $^2\Delta_g$, $^2\Delta_u$ $^2\Sigma_g^-$, $^2\Sigma_u^-$ $^2\Phi_g$, $^2\Phi_u$
N(^{2}P^0) + N$^+$(^{3}P)	3.6	⋯	3.575	$^2\Sigma_g^-$, $^4\Sigma_g^-$ $^2\Sigma_u^-$, $^4\Sigma_u^-$ $^2\Sigma_u^+$, $^4\Sigma_u^+$ $^2\Sigma_g^+$, $^4\Sigma_g^+$ $^2\Pi_u$, $^4\Pi_u$ $^2\Pi_g$, $^4\Pi_g$ $^2\Delta_g$, $^4\Delta_g$ $^2\Delta_u$, $^4\Delta_u$

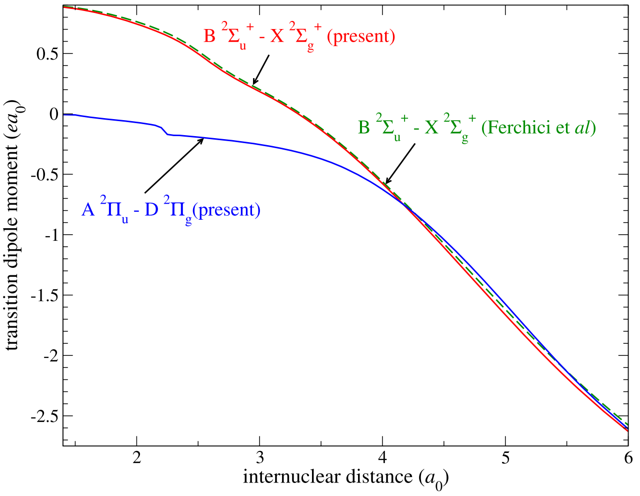

FIG. 5. Matrix elements of dipole moments for X–B and A–D transitions obtained in the present study. The results for the X–B transition are compared to the previous accurate calculations by Ferchichi *et al.*[3]

In N_2^+ molecular plasma, created by an electric discharge or by ionizing radiation, some of the states could be significantly populated: the doublet states, the most likely, significantly more, but quartet and sextet states may also be populated due to N + N^+ collisions and spin-exchange e^-–N_2^+ collisions.

Table I presents the molecular states, for which the PECs were computed in the present study, and compares dissociation energies of these PECs to the previous accurate calculations by Liu *et al.*[2] and experiments, as reported in the NIST database.[6]

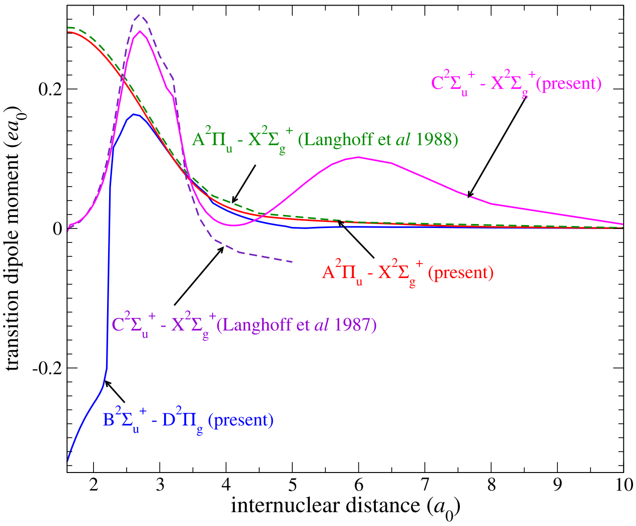

FIG. 6. Matrix elements of dipole moments for the X–A and X–C transitions obtained in this study and compared to the data from the previous calculations by Langhoff *et al.*[7] and Langhoff and Bauschlicher[4] It should be noted that the X and A states dissociate to the first dissociation limit, while the C state dissociates to the second one.

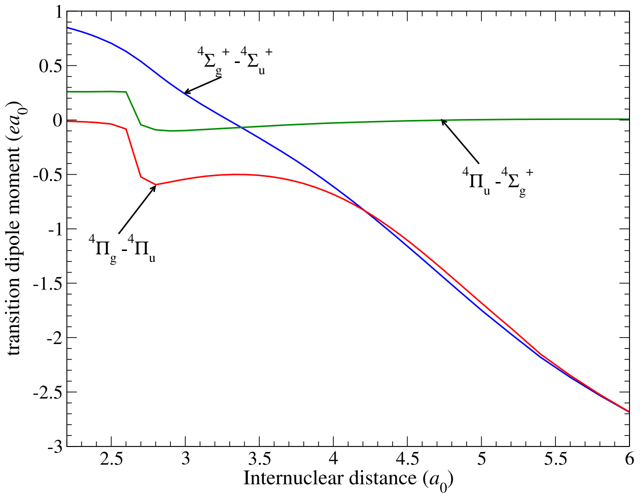

FIG. 7. Matrix elements of dipole moments for transitions between quartet states with PECs dissociating to the first dissociation limit.

For the $N(^4S^0)+N^+(^1D)$ dissociation limit, the present calculations (1.898 eV above the lowest limit) are in better agreement with the experiment than the calculations by Liu *et al.*,[2] while the present results for the $N(^2D^0) + N^+(^3P)$ limit are the same as in Ref. 2.

III. TRANSITION DIPOLE MOMENTS

Together with the PECs, matrix elements of the operator of dipole moment (DM) were evaluated for dipole-allowed transitions for each internuclear distance for which the PECs were computed. The obtained transition dipole moments are available in numerical form in the supplementary material. Figures 5 and 6 compare the present results with the data available from previous calculations. Ferchichi *et al.*[3] computed the DM for transition between the

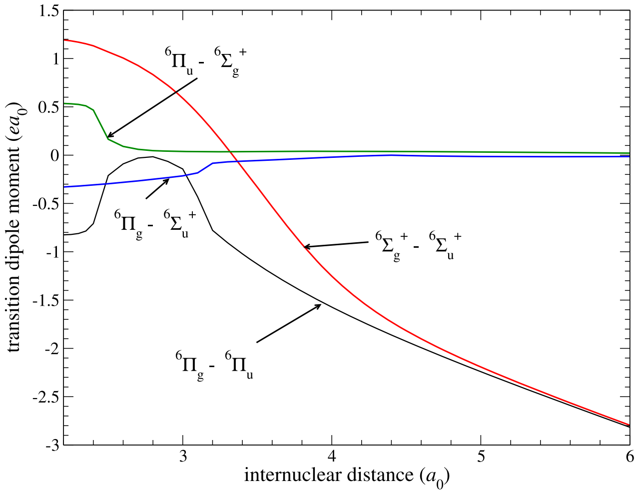

FIG. 8. Matrix elements of dipole moments for transitions between sextet states.

TABLE II. Vibrational energies E and rotational constants B_v of the $X^2\Sigma_g^+$ state, obtained in this study and compared to previous calculations[2,3] and the experiment.[8] The units are in cm^{-1}.

v	E present	E[2]	E[3]	E[8]	B_v present	B_v[2]	B_v[3]	B_v[8]
0	0.00	0.00	0.00	0.00	1.92	1.92	1.92	1.92
1	2 186.74	2 174.33	2 175.62	2 186.30	1.90	1.90	1.90	1.90
2	4 337.7	4 318.73	4 316.12	4 318.10	1.88	1.88	1.88	1.88
3	6 441.6	6 425.42	6 429.17	6 436.9	1.86	1.86	1.86	1.86
4	8 518.55	8 501.9	8 506.64	8 480.9	1.82	1.84	1.84	1.84
5	10 557.72	10 548.60	10 551.06	10 545.49	1.82	1.82	1.82	1.82
6	12 565.34	12 555.78	12 562.02	12 552.20	1.80	1.80	1.80	1.80
7	14 537.83	14 532.26	14 539.71	14 530.10	1.78	1.78	1.78	1.78
8	16 476.75	16 474.58	16 484.00	16 470.80	1.76	1.76	1.76	1.76

TABLE III. Same as presented in Table II but for the $A^2\Pi_u$ state. The energy difference between the ground vibrational levels of the $A^2\Pi_u$ and $X^2\Sigma_g^+$ states is 9823.35 cm^{-1}.

v	E Present	E[2]	E[3]	B_v present	B_v[2]	B_v[8]
0	0.00	0.00	0.00	1.72	1.73	⋯
1	1 874.488	1 874.561	1 873.1	1.71	1.71	⋯
2	3 707.869	3 730.86	3 716.3	1.69	1.69	1.69
3	5 523.317	5 533.704	5 529.6	1.67	1.67	1.67
4	7 300.195	7 318.511	7 313.3	1.65	1.64	1.65
5	9 052.543	9 073.74	⋯	1.63	1.62	1.63
6	10 774.04	10 798.53	⋯	1.60	1.60	1.60
7	12 465.17	12 494.07	⋯	1.59	1.58	1.58
8	14 127.86	14 160.03	⋯	1.57	1.57	1.56

ground state $X^2\Sigma_g^+$ and the $B^2\Sigma_u^+$ state; Langhoff *et al.*[7] reported the TD for the $X^2\Sigma_g^+$–$A^2\Pi_u$ transition; and Langhoff and Bauschlicher[4] computed the DM for the $X^2\Sigma_g^+$–$C^2\Sigma_u^+$ transition. Ferchichi *et al.*[3] have used the MRCI-F12b method in the ACVQZ-F12 basis set, which accounts for all electron correlations taking into account the relativistic correction. It should be noted that the present calculations are in very good agreement with theirs (Fig. 5), although a larger basis set and an *a priori* more accurate method is used by Ferchichi *et al.*[3] For the $A^2\Pi_u$–$X^2\Sigma_g^+$ transition, the present results are somewhat different (see Fig. 6) than previously reported in Ref. 7. In that previous study also, an MRCI method with atomic natural orbitals basis sets was employed. The difference between the results of Ref. 7 and our DMs is attributed to a relative modest basis sets and active space used in the previous study. Figure 6 also compares the present DMs for the X–C transition with the calculations by Langhoff and Bauschlicher,[4] in which a method similar to the one in Ref. 7 was used. Again, the difference between the present DMs and the ones from the previous study is attributed to the modest basis set and active sets used in Ref. 4.

Dipole moments for several other transitions were computed. Figures 7 and 8 show the DMs for transitions between quartet and sextet states. The numerical data for all computed transitions are given in the supplementary material.

IV. VIBRONIC TRANSITION DIPOLE MOMENTS AND EINSTEIN COEFFICIENTS

Having computed the PECs and DMs as functions of the internuclear distance R, we have also calculated the matrix elements for vibronic DMs for allowed transitions evaluating the integral over R,

$$D_{e'v';ev} = \langle \Psi_{e',v'}(R)|D_{e',e}(R)|\Psi_{e,v}(R)\rangle, \qquad (1)$$

where the indices e and e' numerate electronic states and indices v and v' numerate vibrational levels for these electronic states, and

TABLE IV. Same as presented in Table II but for the $B^2\Sigma_u^+$ state, compared to the previous calculations[2,3] and the experiment[9] The energy difference between the ground vibrational levels of the $B^2\Sigma_u^+$ and $X^2\Sigma_g^+$ states is 26 765.20 cm^{-1}.

v	E present	E[2]	E[3]	E[9]	B_v present	B_v[2]	B_v[3]	B_v[9]
0	0.00	0.00	0.00	0.00	2.07	2.07	2.070	2.07
1	2 364.76	2 373.12	2 373.69	2 371.62	2.04	2.05	2.05	2.05
2	4 683.95	4 692.66	4 695.10	4 690.59	2.02	2.02	2.02	2.02
3	6 951.636	6 952.88	6 958.96	6 951.54	1.99	1.99	2.00	2.00
4	9 144.350	9 149.425	9 159.11	9 148.14	1.97	1.97	1.97	1.972
5	11 260.325	11 274.2	11 287.52	11 272.04	1.93	1.93	1.94	1.94
6	13 296.70	13 318.07	13 334.82	13 313.43	1.9	1.9	1.9	1.9
7	15 235.46	17 118.16	15 298.05	15 260.69	1.86	1.86	1.86	1.86
8	17 070.2	18 850.63	17 137.77	17 101.39	1.81	1.81	1.82	1.82

TABLE V. Einstein coefficients for the A(v) → X(v') vibronic transitions. Boldface values are the calculations obtained in the present study, which are compared to data available in the literature.

v' v	0	1	2	3	4	5	6	7
0	**0.398 56(5)**	**0.528 88(5)**	**0.369 22(5)**	**0.189 33(5)**	**0.808 20(4)**	**0.308 71(4)**	**0.109 95(4)**	**0.370 34(3)**
Reference 7	0.4629(5)	0.5696(5)	0.3856(5)	0.1939(5)	0.8173(4)	0.3076(4)	0.1073(4)	0.3545(3)
1	**0.128 48(5)**	**0.205 68(4)**	**0.320 00(5)**	**0.492 77(5)**	**0.400 88(5)**	**0.235 43(5)**	**0.114 42(5)**	**0.495 02(4)**
Reference 7	0.1464(5)	0.3168(4)	0.3682(5)	0.5265(5)	0.4129(5)	0.2383(5)	0.1142(5)	0.4854(4)
2	**0.124 71(4)**	**0.960 38(4)**	**0.165 71(4)**	**0.965 79(4)**	**0.382 51(5)**	**0.490 37(5)**	**0.392 75(5)**	**0.240 60(5)**
Reference 7	0.1374(4)	0.1173(5)	0.1315(4)	0.1249(5)	0.4295(5)	0.5189(5)	0.4016(5)	0.2410(5)
3	**0.310 28(2)**	**0.194 58(4)**	**0.446 78(4)**	**0.649 07(4)**	**0.626 64(3)**	**0.206 87(5)**	**0.442 82(5)**	**0.481 28(5)**
Reference 7	0.3505(2)	0.2299(4)	0.5894(4)	0.6724(4)	0.1265(4)	0.2478(5)	0.4878(5)	0.5031(5)
4	⋯	**0.659 95(2)**	**0.198 70(4)**	**0.123 56(4)**	**0.821 26(4)**	**0.913 24(3)**	**0.718 82(4)**	**0.316 22(5)**
Reference 7	⋯	0.8412(2)	0.2466(4)	0.1879(4)	0.9245(4)	0.5673(3)	0.9586(4)	0.3605(5)
5	⋯	⋯	**0.902 33(2)**	**0.160 97(4)**	**0.738 48(2)**	**0.684 32(4)**	**0.431 47(4)**	**0.833 58(3)**
Reference 7	⋯	⋯	0.1230(3)	0.2098(4)	0.2105(3)	0.8209(4)	0.4010(4)	0.1633(4)
6	⋯	⋯	⋯	**0.958 45(2)**	**0.110 47(4)**	**0.124 23(3)**	**0.427 20(4)**	**0.692 39(4)**
Reference 7	⋯	⋯	⋯	0.1395(3)	0.1518(4)	0.5729(2)	0.5510(4)	0.7151(4)
7	⋯	⋯	⋯	⋯	**0.857 95(2)**	**0.650 37(3)**	**0.580 99(3)**	**0.196 90(4)**
Reference 7	⋯	⋯	⋯	⋯	0.1343(3)	0.9544(3)	0.5156(3)	0.2830(4)

$D_{e',e}(R)$ is the electronic R-dependent DM matrix element between states e and e'. For de-excitation vibronic transitions, when the energy E_{ev} of the initial level is above the energy of the final level $E_{e'v'}$, we have also computed Einstein coefficients for spontaneous photon emission,

$$A_{e'v' \leftarrow ev} = \frac{4}{3}\frac{\left(E_{ev} - E_{e'v'}\right)^3}{\hbar^4 c^3}\left|D_{e'v';ev}\right|^2. \tag{2}$$

The coefficients for the dipole-allowed transitions between the vibronic levels of the lowest doublet states and for one quarter pair

TABLE VI. Einstein coefficients for the B(v) → X(v') vibronic transitions. Boldface values are the calculations obtained in the present study, which are compared to data available in the literature.

v' v	0	1	2	3	4	5	6	7
0	**0.118 82(8)**	**0.588 95(7)**	**0.879 78(6)**	**0.338 28(5)**	**0.237 06(2)**	**0.127 81(3)**	**0.312 50(1)**	**0.139 40**
Reference 3	0.121 20(8)	0.635 85(7)	1.042 2(6)	0.485 38(5)	0.200 28(1)	0.154 60(3)	0.282 61(1)	0.599 42
1	**0.373 57(7)**	**0.443 35(7)**	**0.811 68(7)**	**0.201 27(7)**	**0.868 71(5)**	**0.115 25(4)**	**0.866 33(3)**	**0.486 35**
Reference 3	0.390 87(7)	0.426 13(7)	0.864 39(7)	0.239 24(7)	0.130 51(6)	0.450 79(3)	0.100 06(4)	0.171 32(1)
2	**0.757 78(6)**	**0.435 64(7)**	**0.118 33(7)**	**0.847 57(7)**	**0.308 63(7)**	**0.122 27(6)**	**0.929 44(4)**	**0.239 12(4)**
Reference 3	0.8122(6)	0.450 68(7)	0.975 52(6)	0.882 20(7)	0.364 65(7)	0.198 94(6)	0.605 91(4)	0.313 18(4)
3	**0.125 30(6)**	**0.152 91(7)**	**0.365 34(7)**	**0.110 05(6)**	**0.800 14(7)**	**0.389 55(07)**	**0.105 68(6)**	**0.372 80(5)**
Reference 3	0.136 44(6)	0.163 10(7)	0.368 91(7)	0.413 62(5)	0.812 38(7)	0.460 87(7)	0.203 98(7)	0.310 40(5)
4	**0.184 10(5)**	**0.364 92(6)**	**0.201 97(7)**	**0.258 68(7)**	**0.376 68(5)**	**0.731 86(7)**	**0.432 46(7)**	**0.401 10(5)**
Reference 3	0.201 69(5)	0.394 98(6)	0.251 66(7)	0.212 55(7)	0.112 21(6)	0.726 18(7)	0.519 23(7)	0.1239(6)
5	**0.248 81(4)**	**0.703 10(5)**	**0.651 52(6)**	**0.216 76(7)**	**0.160 52(7)**	**0.265 80(6)**	**0.680 30(7)**	**0.432 64(7)**
Reference 3	0.271 243(4)	0.769 96(5)	0.698 96(6)	0.224 75(7)	0.148 99(7)	0.446 48(6)	0.660 95(7)	0.532 46(7)
6	**0.314 24(3)**	**0.118 63(5)**	**0.158 94(6)**	**0.910 04(6)**	**0.204 13(7)**	**0.895 27(6)**	**0.451 54(6)**	**0.659 89(7)**
Reference 3	0.341 68(3)	0.130 48(5)	0.172 65(6)	0.967 56(6)	0.208 71(7)	0.771 39(6)	0.690 71(6)	0.633 55(7)
7	**0.368 11(2)**	**0.182 70(4)**	**0.325 18(5)**	**0.273 55(6)**	**0.108 38(7)**	**0.176 68(7)**	**0.453 86(6)**	**0.471 42(6)**
Reference 3	0.398 12(2)	0.199 17(4)	0.356 48(5)	0.294 28(6)	0.114 66(7)	0.177 49(7)	0.345 66(6)	0.719 13(6)

TABLE VII. Einstein coefficients for the C(v) → X(v') vibronic transitions. Boldface values are the calculations obtained in the present study, which are compared to data available in the literature.

v' v	0	1	2	3	4	5	6	7
0	**0.691 15(5)**	**0.486 75(6)**	**0.154 35(7)**	**0.285 62(7)**	**0.336 26(7)**	**0.262 49(7)**	**0.134 33(6)**	**0.412 00(6)**
Reference 7	0.136(6)	0.896(6)	0.256(7)	0.411(7)	0.406(7)	0.249(7)	0.910(6)	0.173(6)
1	**0.264 37(6)**	**0.107 04(7)**	**0.144 75(7)**	**0.474 99(6)**	**0.143 33(6)**	**0.203 60(7)**	**0.355 10(7)**	**0.258 06(7)**
Reference 7	…	…	…	…	…	…	…	…
2	**0.492 05(6)**	**0.943 54(6)**	**0.209 76(6)**	**0.310 11(6)**	**0.617 67(6)**	**0.341 99(7)**	**0.367 12(7)**	**0.137 34(7)**
Reference 7	0.651(6)	0.1007(7)	0.116(6)	0.602(6)	0.134(7)	0.502(5)	0.181(7)	0.527(7)
3	**0.593 91(6)**	**0.425 71(6)**	**0.499 21(5)**	**0.700 32(6)**	**0.113 12(6)**	**0.507 22(6)**	**0.821 22(6)**	**0.627 23(5)**
4	**0.566 44(6)**	**0.802 10(5)**	**0.310 65(6)**	**0.232 04 (6)**	**0.197 81(6)**	**0.586 71(6)**	**0.164 45(5)**	**0.866 92(6)**
5	**0.474 37(6)**	**0.913 37(3)**	**0.353 36(6)**	**0.817 02(2)**	**0.429 00(6)**	**0.178 22(5)**	**0.514 23(6)**	**0.110 42(6)**
6	**0.354 01(6)**	**0.656 82(5)**	**0.199 55(6)**	**0.107 84(6)**	**0.185 01(6)**	**0.170 69(6)**	**0.272 45(6)**	**0.174 68 (6)**
7	**0.241 44(6)**	**0.149 67(6)**	**0.496 32(5)**	**0.213 95(6)**	**0.529 13(4)**	**0.297 48(6)**	**0.367 23(3)**	**0.396 60(6)**

TABLE VIII. Einstein coefficients for the D(v) → A(v') vibronic transitions. Boldface values are the calculations obtained in the present study.

v' v	0	1	2	3	4	5	6	7
0	**0.288 35(2)**	**0.408 42(3)**	**0.283 22(4)**	**0.124 40(5)**	**0.389 66(5)**	**0.924 66(5)**	**0.172 33(6)**	**0.258 93(6)**
1	**0.236 01(3)**	**0.286 62(0)**	**0.166 34(5)**	**0.592 69(5)**	**0.144 44(6)**	**0.251 41(6)**	**0.314 73(6)**	**0.274 82(6)**
2	**0.102 65(4)**	**0.106 67(5)**	**0.514 75(5)**	**0.146 57(6)**	**0.269 13(6)**	**0.319 92(6)**	**0.225 39(6)**	**0.642 47(5)**
3	**0.315 93(4)**	**0.280 20(5)**	**0.111 53(6)**	**0.248 76(6)**	**0.327 53(6)**	**0.231 22(6)**	**0.512 01(5)**	**0.889 37(4)**
4	**0.772 43(4)**	**0.583 04(5)**	**0.189 51(6)**	**0.322 05(6)**	**0.279 86(6)**	**0.819 94(5)**	**0.410 79(4)**	**0.113 91(6)**
5	**0.159 69(5)**	**0.102 23(6)**	**0.267 95(6)**	**0.333 36(6)**	**0.162 98(6)**	**0.223 48(4)**	**0.848 49(5)**	**0.157 93(6)**
6	**0.290 31(5)**	**0.157 01(6)**	**0.326 54(6)**	**0.279 79(6)**	**0.515 88(5)**	**0.299 29(5)**	**0.159 03(6)**	**0.858 19(5)**
7	**0.476 81(5)**	**0.216 84(6)**	**0.350 45(6)**	**0.186 79(6)**	**0.119 97(4)**	**0.109 01(6)**	**0.145 12(6)**	**0.942 37(4)**

(${}^4\Sigma_g^+ + (v) \to {}^4\Sigma_u^+ + (v')$) are presented in Tables V–IX. For the A(v') → X(v), B(v) → X(v'), C(v) → X(v'), and D(v) → A(v') transitions, we have compared the present results to the previous calculations. Tables II–IV provide energies and rotational constants of a few vibrational levels of the three lowest doublet states $X^2\Sigma_g^+$, $A^2\Pi_u$, and $B^2\Sigma_u^+$ and compare them to the experimental data by Lofthus and Krupenie[8] and Klynning and Pages[9] and the most accurate available theoretical data by Liu *et al.*[2] and Ferchichi *et al.*[3] As one can see, the present calculations agree with the experiment within a few wavenumbers. It should be noted that for the lowest vibrational levels, the calculations by Liu *et al.*[2] agree better with the experiment than ours (see, for example, v = 0–6 of the B state),

TABLE IX. Einstein coefficients for the ${}^4\Sigma_g^+(v) \to {}^4\Sigma_u^+(v')$ transitions. Boldface values are the calculations obtained in the present study.

v' v	0	1	2	3	4	5	6	7
0	**0.259 71(2)**	**0.214 30(3)**	**0.104 29(4)**	**0.330 73(4)**	**0.723 27(4)**	**0.108 12(5)**	**0.310 076(5)**	**0.412 77(4)**
1	**0.428 32(3)**	**0.255 29(4)**	**0.985 01(4)**	**0.246 64(5)**	**0.421 61 (5)**	**0.482 68(5)**	**0.342 06(5)**	**0.121 48(5)**
2	**0.407 78(4)**	**0.158 21(5)**	**0.476 77(5)**	**0.904 74(5)**	**0.114 80(6)**	**0.907 55(5)**	**0.387 75(5)**	**0.571 38(4)**
3	**0.333 92(5)**	**0.658 42(5)**	**0.159 38(6)**	**0.210 52(6)**	**0.184 87(6)**	**0.816 52(5)**	**0.103 39(5)**	**0.121 08(4)**
4	**0.423 96(6)**	**0.135 43(6)**	**0.472 14(6)**	**0.280 45(6)**	**0.180 22(6)**	**0.157 00(5)**	**0.393 83(4)**	**0.208 22(5)**
5	**0.206 56(8)**	**0.412 22(7)**	**0.267 20(7)**	**0.665 81(6)**	**0.204 66(6)**	**0.130 94(6)**	**0.124 29(5)**	**0.104 45(5)**
6	**0.488 03(6)**	**0.242 41(7)**	**0.331 30(5)**	**0.772 81(6)**	**0.137 34(4)**	**0.231 07(4)**	**0.695 98(5)**	**0.107 23(5)**

but for higher levels (see, for example, $v = 7$–8 of the B state), the accuracy of the results in Ref. 2 drops significantly. This is due to a particular basis set used by Liu *et al.*,[2] which is not adapted for large internuclear separations in N_2^+: the significant decrease in accuracy of energies of the excited vibrational levels in Ref. 2 is associated with the loss of accuracy of PECs at large internuclear distances.

V. CONCLUSION

Concluding the present study, we would like to stress the following findings.

- This study has provided the accurate data needed for modeling behavior of the N_2^+ plasma in the presence of radiation.
- Potential energy curves of the 36 lowest electronic states of the N_2^+ molecular ion were computed. In the calculation of the electronic states, dissociating to the lowest threshold, relativistic corrections were also accounted for.
- Vibrational levels in the electronic states were also calculated. Comparing with experimental data, the accuracy of the obtained vibronic levels is within 2–20 cm^{-1}. Therefore, the estimated uncertainty of the computed PECs is of that order. The disagreement with the experimental results could be attributed to non-Born–Oppenheimer effects, which are not accounted for in this study.
- Transition dipole moments between the electronic states and vibronic levels were also computed. Compared to dipole moments, available for three electronic transitions from previous studies, an agreement is better than 1%,[3] within 2%,[4] and about 10%.[7] The estimated accuracy of the DM, obtained in this study, is better than 1% for the lowest electronic states.
- The data obtained in this study are available in electronic form in the supplementary material.

SUPPLEMENTARY MATERIAL

Data files containing the potential energy curves for all the electronic states and the results with and without relativistic corrections are provided in the supplementary material. In addition, we have included the results for the electronic transition dipole moments and the vibronic moments.

ACKNOWLEDGMENTS

The authors acknowledge support from the Transatlantic Mobility Program and Chateaubriand Fellowship of the Office for Science and Technology of the Embassy of France in the United States, the Programme National “Physique et Chimie du Milieu Interstellaire” (PCMI) of CNRS/INSU, the program “Accueil des chercheurs étrangers” of CentraleSupélec, the ADI “Programme de financement des cotutelles internationales de doctorat” of Université Paris-Saclay, and the National Science Foundation, Grant Nos. 2110279 and 2409570 (UCF). This work benefited from French state aid under France 2030 (QuanTEdu-France) bearing the reference ANR-22-CMAS-0001. We thank Alexander Alijah for providing us with the B–X transition dipole moments from Ref. 3 and Ioan F. Schneider.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Chaima Hammami: Data curation (equal); Formal analysis (equal); Investigation (equal); Visualization (equal); Writing – original draft (equal). **Conner Penson**: Data curation (equal); Investigation (equal); Visualization (equal). **Mehdi Adrien Ayouz**: Conceptualization (equal); Funding acquisition (equal); Methodology (equal); Project administration (equal); Resources (equal); Supervision (equal); Validation (equal); Writing – review & editing (equal). **Viatcheslav Kokoouline**: Data curation (equal); Formal analysis (equal); Methodology (equal); Resources (equal); Visualization (equal); Writing – review & editing (equal).

DATA AVAILABILITY

All computed data are available in the form of tables and supplementary material.

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