

## Sign reversal of the spin-orbit constant for the $C\ 3\ u$ state of $N\ 2$

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# Sign reversal of the spin-orbit constant for the $C^3\Pi_u$ state of $N_2$

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*Ab initio* calculations are performed at the multireference configuration-interaction level of theory on the diagonal spin-orbit functions for the lowest non-Rydberg states of  $^3\Pi_u$  symmetry in molecular nitrogen. Spin-orbit constants deduced from the *ab initio* results confirm the recent suggestion, based on new experimental results, that the  $C^3\Pi_u$  state of  $N_2$ , long known to be *regular* in the region of its potential-energy curve minimum, becomes *inverted* at higher energies. By removing the effects of the crossing  $C'^3\Pi_u$  state, it is shown that  $A_v$  for the  $C$  state changes sign from positive to negative near  $v=8$ , corresponding to a change in principal molecular-orbital configuration from  $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)(3\sigma_g)^2(1\pi_u)^4(1\pi_g)$  to  $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g) \times (1\pi_u)^3(1\pi_g)^2$  at an internuclear distance near 1.4 Å. © 2008 American Institute of Physics. [DOI: 10.1063/1.2990658]

## I. INTRODUCTION

The structure and predissociation dynamics of the coupled  $^3\Pi_u$  states of  $N_2$  are key drivers controlling  $N_2$  dissociation, which is a significant process in the photochemistry of nitrogen-rich planetary atmospheres. In particular, the  $C^3\Pi_u$  state, itself heavily predissociated above  $\sim 100\,000\text{ cm}^{-1}$  by the continuum of the  $C'^3\Pi_u$  state, is known to control the predissociation of the lowest dipole-accessible  $^1\Pi_u$  states of  $N_2$  through spin-orbit coupling to the  $b^1\Pi_u$  state.<sup>1</sup>

The  $C^3\Pi_u$  state of  $N_2$  has been known for many years,<sup>2</sup> not only from transitions of the  $C^3\Pi_u-B^3\Pi_g$  second-positive system in emission, but also those of the  $C^3\Pi_u-X^1\Sigma_g^+$  Tanaka system in absorption. In the region of its potential-energy curve minimum, the  $\sigma_u\pi_g$  principal molecular-orbital (MO) configuration of the valence-hole  $C$  state implies that this state will be *regular*, with a diagonal spin-orbit parameter  $A > 0$ .<sup>3</sup> Indeed, analyses of experimental second-positive spectra by Budó<sup>4</sup> indicate that  $A_v$  decreases from +39.0 to +34.5  $\text{cm}^{-1}$  as  $v$  increases from 0 to 4.

The spectroscopy of the  $C$  state is complicated at higher energies by an electrostatic interaction with the  $C'^3\Pi_u$  valence state since the inner limb of the  $C'$ -state potential crosses the outer limb of the  $C$ -state potential at an energy between the  $C(v=5)$  and  $(v=6)$  levels, leading to significant perturbations. This interaction has been studied extensively, starting with the insightful work of Carroll and Mulliken.<sup>5</sup> In particular, experimental studies by Ledbetter and Dressler<sup>6</sup> and Ledbetter<sup>7</sup> confirmed a strong interaction between  $C(v=5)$  and  $C'(v=1)$ . In this case, a *two-level-deperturbed*  $A_5 = +33\text{ cm}^{-1}$  has been estimated for the  $C$  state,<sup>6</sup> consistent

with the trend exhibited by the lower- $v$  levels.

Very recently, in the first companion paper of this work,<sup>8</sup> several previously unknown higher levels of the  $C$  state were characterized spectroscopically, either through their direct observation in dipole-forbidden transitions from the ground state and/or, indirectly, through their perturbative effects on the dipole-accessible states of  $N_2$ . Because of the nature of these observations, it was impossible, unambiguously, to determine the sense of the associated spin-orbit splittings since the usual robust technique of noting in which triplet subband the missing low-rotational lines occur was unavailable. However, using qualitative arguments, Lewis *et al.*<sup>8</sup> claimed that a *negative*  $A$ -value in the particular case of the  $C(v=14)$  level of  $^{15}N_2$  provided better agreement with the detailed observed spectroscopy of this level. Thus, the interesting prospect of a change in the character of the  $C$  state from regular to inverted, somewhere between  $v=5$  and  $v=14$ , is raised.

At present, there is insufficient guidance from *ab initio* calculations to shed light on this issue. Several *ab initio* calculations of potential-energy curves for the non-Rydberg  $^3\Pi_u$  states of  $N_2$  have been performed over the years,<sup>9-13</sup> with only limited publication in the open literature. The most recent multireference configuration-interaction (MRCI) (plus Davidson correction) calculations by Partridge<sup>13</sup> displayed an inflection near an internuclear distance  $R=1.5\text{ Å}$  in the second  $^3\Pi_u$  potential-energy curve (i.e., on the outer limb of the  $C$  state), indicating a significant MO configurational change, which is of central importance to the present work. On the other hand, as far as we are aware, there has only been a single *ab initio* calculation of a diagonal spin-orbit function for the  $^3\Pi_u$  states of  $N_2$ , specifically for the lowest adiabatic state  $C-C'$ , by Robbe,<sup>14</sup> for a limited range of  $R$ .

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Therefore, the aim of the present work is to perform *ab initio* calculations of the diagonal spin-orbit functions  $A(R)$  for the lowest few non-Rydberg states of  ${}^3\Pi_u$  symmetry, to enable the construction of a realistic spin-orbit function for the  $C$  state, over an extended range of  $R$ , in order that the hypothesis of Ref. 8, regarding the possible sign reversal of  $A_v$ , might be tested.

## II. CALCULATIONS

In a pioneering work on the feasibility of computing the dipole-accessible mixed valence-Rydberg states of  ${}^1\Pi_u$  and  ${}^1\Sigma_u^+$  symmetry in  $N_2$ , Spelsberg and Meyer<sup>15</sup> evaluated the performance of a variety of *ab initio* techniques. They showed that the computation of such states is nontrivial, requiring special care in order to obtain realistic results. Here, we use a similar approach which is, nevertheless, adapted to the computation of the non-Rydberg  ${}^3\Pi_u$  states of  $N_2$ . These electronic calculations are performed using the MOLPRO program suite,<sup>16</sup> in the  $D_{2h}$  point group since MOLPRO does not consider the  $D_{\infty h}$  point group. The nitrogen atoms are described using the generally contracted aug cc-pVQZ basis set of Dunning<sup>17</sup> which is augmented by three  $s$  and two  $p$  diffuse Gaussian-type orbitals (GTOs), resulting in 178 contracted GTOs to be considered.

Because of the multiconfigurational nature of the electronic states of interest here, only configuration-interaction methods can be used. Therefore, we employ the complete-active-space self-consistent-field<sup>18</sup> (CASSCF) and the internally contracted MRCI (Refs. 19 and 20) techniques. In addition to the valence orbitals, the CASSCF active space is augmented by one  $\sigma_g$  and one  $\pi_g$  MO, hence ensuring orbital relaxation between the  ${}^3\Pi_u$  group of states whose configurations differ in their  $\sigma/\pi$  orbital occupations. This leads to 12 270 configuration state functions (CSFs) in the  ${}^3B_{2u}$  and  ${}^3B_{3u}$  symmetries. Moreover, four electronic states (three  ${}^3\Pi_u$  and a close lying  ${}^3\Phi_u$  state) are averaged together using the CASSCF averaging procedure implemented in MOLPRO, where four  ${}^3B_{2u}$  and four  ${}^3B_{3u}$  components are considered. Then, all CSFs from the CASSCF approach are taken as the reference in the MRCI calculations, where more than  $2.6 \times 10^8$  CSFs for each symmetry are considered. All electrons are correlated.

Finally, the spin-orbit matrix elements are evaluated in Cartesian coordinates using the CASSCF wave functions and a smaller basis set, i.e., the *spdf* cc-pVQZ basis subset.<sup>17</sup> The quality of these matrix elements is less dependent on the particular *ab initio* method so they can be computed at a lower level of theory.<sup>21</sup>

## III. RESULTS AND DISCUSSION

The calculated MRCI potential-energy curves for the lowest three non-Rydberg states of  ${}^3\Pi_u$  symmetry in  $N_2$  are shown in Fig. 1, labeled  $C$ - $C'$ ,  $C'$ - $C$ -III, and III- $C$ , respectively, where the labels  $C$ ,  $C'$ , and III refer to our adopted crossing (“diabatic”) potentials. The present *ab initio* potentials are similar to those from other MRCI calculations,<sup>11–13</sup> but differ in detail, e.g., in the strengths of the avoided crossings. The complex behavior exhibited in Fig. 1 may be

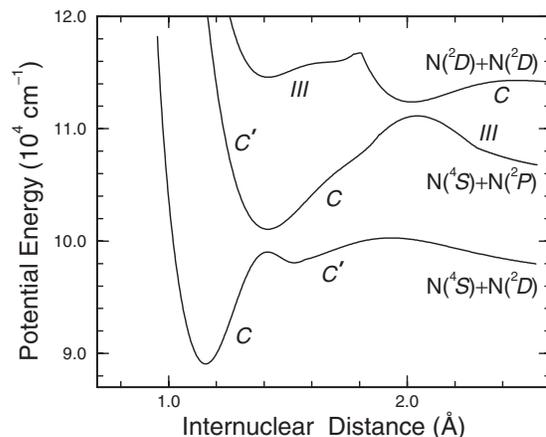


FIG. 1. Calculated MRCI potential-energy curves for the lowest three non-Rydberg states of  ${}^3\Pi_u$  symmetry in  $N_2$ . Segments of the adiabatic potentials are labeled in accordance with the nomenclature adopted for the crossing (diabatic) states considered in the text. The energy scale is referenced to the  $v=0, J=0$  level of the  $X\ {}^1\Sigma_g^+$  ground state (not shown). The lowest dissociation limit,  $N({}^4S)+N({}^4S)$ , is beyond the scale of the figure.

thought of, in the lowest order, as due to interactions between the strongly bound valence-hole MO configuration  $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)(3\sigma_g)^2(1\pi_u)^4(1\pi_g)$  ( $R_e \approx 1.15$  Å), the bound valence configuration  $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)(1\pi_u)^3(1\pi_g)^2$  ( $R_e \approx 1.55$  Å), which gives rise to four  ${}^3\Pi_u$  states,<sup>5</sup> and configurations containing the strongly antibonding  $3\sigma_u$  orbital. In the adiabatic picture provided by the *ab initio* calculations, there are two avoided crossings in Fig. 1, near 1.4 and 2.0 Å. In the present work, we are interested primarily in the properties of the  $C$   ${}^3\Pi_u$  state, i.e., the deepest potential well in Fig. 1, which correlates with the  $N({}^2D)+N({}^2D)$  dissociation limit (the avoided crossings on its outer limb having been removed). In this picture, this  $C$ -state potential is crossed by the weakly bound  $C'$ -state potential which correlates with the  $N({}^4S)+N({}^2D)$  limit, and by a repulsive potential, labeled III, which correlates with the  $N({}^4S)+N({}^2P)$  limit. Approximate crossing potentials can be constructed from the calculated adiabatic potential-energy curves in Fig. 1 by smoothly connecting the appropriately labeled segments, but we note that such potentials are not fully diabatic, according to the strict definition of the term. Nevertheless, they are extremely useful in the construction of realistic coupled-channel models of  $N_2$  spectroscopy and predissociation dynamics.<sup>1</sup>

The calculated diagonal spin-orbit functions for the lowest non-Rydberg states of  ${}^3\Pi_u$  symmetry in  $N_2$ , labeled consistently with the corresponding MRCI potential-energy curves of Fig. 1, are shown in Fig. 2 (connected symbols). It is evident that the spin-orbit function for the  $C$  state (solid curve), which has been approximated by smoothly joining the three adiabatic segments marked  $C$  in Fig. 2, changes sign dramatically near 1.4 Å. This represents the key result of the present study. For  $R \leq 1.3$  Å, where the  $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)(3\sigma_g)^2(1\pi_u)^4(1\pi_g)$  valence-hole MO configuration is dominant, the  $C$  state is regular, with  $A(R)$  reaching  $+33$   $\text{cm}^{-1}$ . On the other hand, for  $1.6 \leq R \leq 2.2$  Å, where the  $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g) \times (1\pi_u)^3(1\pi_g)^2$  valence configuration dominates, it is in-

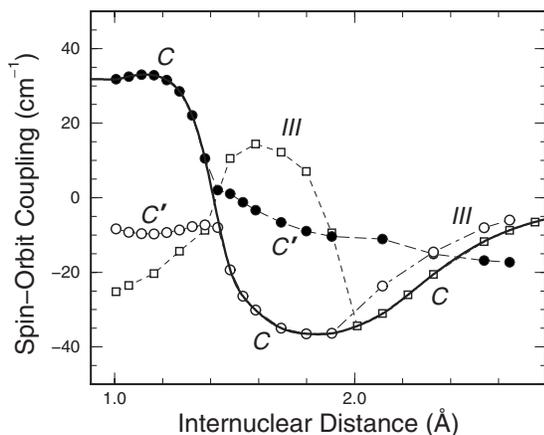


FIG. 2. Calculated *ab initio* diagonal spin-orbit functions for the lowest three non-Rydberg states of  ${}^3\Pi_u$  symmetry in  $N_2$ , with adiabatic segments labeled correspondingly with the nomenclature of Fig. 1. Solid circles, long-dashed curve: lowest adiabatic state. Open circles, dot-dashed curve: second adiabatic state. Open squares, dashed curve: third adiabatic state. The adjoined spin-orbit function for the C state is shown as the solid curve.

verted, with  $A(R)$  reaching  $-36\text{ cm}^{-1}$ . Of the four  ${}^3\Pi_u$  states arising from this latter configuration, two are expected to be regular and two inverted.<sup>5</sup> Evidently, the mixing between these states is dominated by the inverted states, in the case of the outer limb of the C state. In contrast, the  $C'$  state, which arises from the same MO configuration, has a much smaller  $A(R)$ , over the full range of  $R$ , indicating that it is dominated by a more even mixture of the regular and inverted  ${}^3\Pi_u$  states. Finally, as  $R$  increases beyond  $\sim 2.2\text{ Å}$ , extensive configuration mixing results in  $A(R)$  asymptoting to zero.

In order to compare with experiment, it is necessary to transform the *ab initio* spin-orbit function  $A(R)$  for the C state into appropriate spin-orbit constants  $A_v$ . As has been discussed in detail in the second companion paper of this work,<sup>22</sup> the strong couplings within the  ${}^3\Pi_u$  manifold, including the  $3s\sigma_g F_3\ {}^3\Pi_u$  and  $3p\pi_u G_3\ {}^3\Pi_u$  Rydberg states (not included in the present calculations) normally mandate coupled-channel calculations for an accurate spectroscopic description of  $N_2$ . However, as mentioned in Ref. 22, most of the C-state levels are relatively unmixed. Furthermore, the levels for which comparisons with experiment are possible are mostly well away from the  $C\sim C'$  crossing region. Therefore, for the purposes of the present study, it is sufficient to make a single-potential approximation and ignore the C-state couplings. Using the present *ab initio*-based  $A(R)$  for the C state (solid curve in Fig. 2), together with vibrational wave functions  $\chi_v(R)$  for the diabatic-model C-state potential-energy curve of Ref. 22 computed using the renormalized Numerov method,<sup>23</sup> spin-orbit constants have been calculated using the relation  $A_v = \langle \chi_v(R) | A(R) | \chi_v(R) \rangle$ . The results, plotted in Fig. 3 as a solid curve, are compared with the experimental values (circles), taken from Refs. 4, 6, and 8, also including an additional value for  $C(v=9)$ ,  ${}^{14}N_2$  obtained by reinterpreting the results of Ref. 24.<sup>25</sup> In order to compare with all of the available experimental data, we have combined results for the  ${}^{14}N_2$  (closed circles) and  ${}^{15}N_2$  (open circles) isotopomers in Fig. 3, plotting the spin-orbit constants as a function of  $\rho(v+1/2)$ , where  $\rho = \sqrt{\mu_{14}/\mu_{15}}$  and the

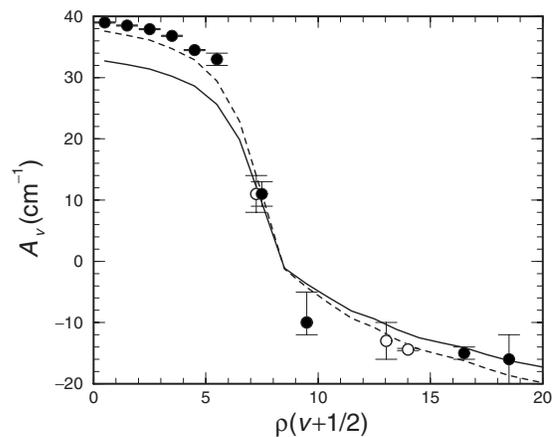


FIG. 3. Comparison between calculated and experimental diagonal spin-orbit constants  $A_v$  for the C  ${}^3\Pi_u$  state of  $N_2$ , plotted as a function of the mass-reduced vibrational quantum number. Solid circles: experimental values for  ${}^{14}N_2$ , from Refs. 4, 6, 8, 24, and 25 (see text). Open circles: experimental values for  ${}^{15}N_2$ , from Ref. 8. Solid curve: present calculated results. Dashed curve: present results, scaled by a factor of 1.15.

$\mu_i$  are the respective isotopic reduced molecular masses. The good agreement between the *ab initio*-based and experimental results clearly confirms the contention in Ref. 8 that the diagonal spin-orbit constants for the C( $v$ ) levels change sign from positive to negative as  $v$  increases, the calculations showing that the zero crossing occurs near  $v=8$ . Even better overall agreement is obtained if the calculations are scaled by a factor of 1.15, with no  $R$ -shift being necessary.

Finally, we note that a value  $A_0 = 1.15\text{ cm}^{-1}$  was determined by Carroll<sup>26</sup> for the  $C'(v=0)$  level, from rotational analyses of the  $C'\ {}^3\Pi_u - B\ {}^3\Pi_g(0, v'')$  Goldstein-Kaplan bands, implying effectively Hund's case-(b) angular-momentum coupling. This level lies very close to the  $C-C'$  crossing region, sampling  $R$  values centered on  $1.517\text{ Å}$ . In this region, an inspection of Fig. 2 shows that the adiabatic  $A(R)$  values for the  $C'$ -state segments do not connect smoothly. Thus, the single-potential approximation, used above for the C( $v$ ) levels, which ignores the effects of off-diagonal couplings, is likely to be invalid in the region of  $C'(v=0)$ . The MRCI  $A(R)$  value for the lowest adiabatic  ${}^3\Pi_u$  state at  $R = 1.517\text{ Å}$  is  $\sim -0.4\text{ cm}^{-1}$ , not too far from the experimental value and supporting the observation of case-(b) coupling for  $C'(v=0)$ .

#### IV. SUMMARY AND CONCLUSIONS

*Ab initio* calculations have been performed at the MRCI level of theory on the diagonal spin-orbit functions for the lowest non-Rydberg states of  ${}^3\Pi_u$  symmetry in molecular nitrogen. Spin-orbit constants deduced from the *ab initio* results confirm the recent suggestion, based on new experimental results,<sup>8</sup> that the C  ${}^3\Pi_u$  state of  $N_2$ , long known to be regular in the region of its potential-energy curve minimum, becomes *inverted* at higher energies. By removing the effects of the crossing  $C'\ {}^3\Pi_u$  state, it is shown that  $A_v$  for the C state changes sign from positive to negative near  $v=8$ , in association with a change in principal MO configuration from  $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)(3\sigma_g)^2(1\pi_u)^4(1\pi_g)$  to  $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)(1\pi_u)^3(1\pi_g)^2$  at an internu-

clear distance near 1.4 Å. The present *ab initio* results are consistent with the sign choices for  $A_v$  adopted in the experimental data analyses of Ref. 8, the first companion paper of this work.

## ACKNOWLEDGMENTS

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<sup>25</sup>In Ref. 24, a coupled-channel study of rotational predissociation linewidths for the  $b^1\Pi_u(v=3)$  level of  $^{14}\text{N}_2$  provided constraints on the value of the spin-orbit constant for the  $C(v=9)$  level, assuming that  $A_9$  was positive. Following the new experimental results of Ref. 8, it is likely that this assumption was incorrect. Therefore, the results of Ref. 24 have been reinterpreted, assuming a negative value for  $A_9$ , providing the additional data point in Fig. 3,  $-10_{-2}^{+5}$ . The asymmetric error bar arises because of a rapidly decreasing sensitivity of the linewidths to  $A$ -values which approach zero.

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