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APPLICATION OF QUANTUM CHEMISTRY TO ATMOSPHERIC CHEMISTRY.(U)
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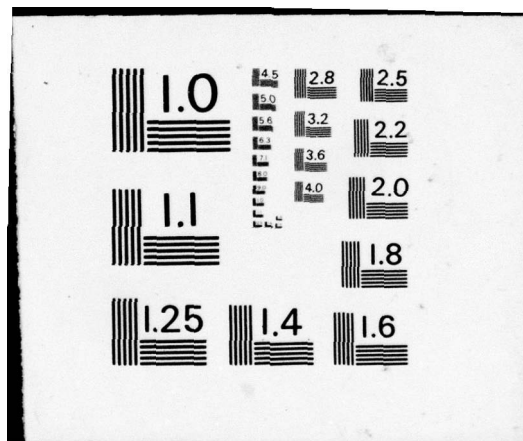
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Annual Report: FY 1976

Application of Quantum Chemistry to Atmospheric Chemistry

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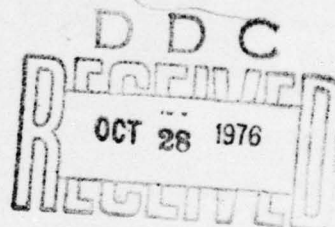
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Annual Report: FY 1976

Application of Quantum Chemistry to Atmospheric Chemistry

I. Introduction

The excitation of nitrogen and oxygen molecules is the primary event in the excitation of the atmosphere. We are continuing our theoretical calculations of the electronic properties of these molecules required for the prediction of optical emissions from normal and disturbed atmospheres. The last year we attempted a theoretical analysis of the predissociation line broadening in the Schumann-Runge bands of O_2 . There was some differences between the calculated and experimental widths for a small range of vibrational levels. These have now been resolved and rather complete theoretical understanding is now in hand for the predissociation of O_2 in the Schumann-Runge bands.

The analysis of the electronic structure of excited states of nitrogen has also continued. The $5\Sigma_g^+$ state is central to all kinetic theories of the nitrogen afterglow and the energy curves of the two lowest $5\Sigma_g^+$ states have been determined using the multi-configuration self-consistent-field method. This study has improved our understanding of the interaction of two nitrogen atoms and the general problem of electronic reorganization during bond formation or dissociation.

We have obtained multi-configurational wavefunctions for the C and C' $3\Pi_u$ states, the B $3\Pi_g$ state, and the X $1\Sigma_g^+$ states of N_2 . Using these wavefunctions the radiative transition probabilities have been calculated and the electron impact cross section calculations are in progress. The necessity of using a multi-configurational approach is confirmed by the

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complexity of the wavefunction for the $^3\Pi_u$ states and the complex shape of the transition probability curves.

The Rydberg states of the $^2\Sigma_g^+$ and $^2\Pi_u$ ions are also being modelled using single configuration wavefunctions. The singlet diabatic Rydberg states have been modelled by Dressler and Leoni who estimated the energy positions of the F and G $^3\Pi_u$ states. The present results suggest a slightly higher energy position for the F $^3\Pi_u$ state.

The electronic structure of these states will be analyzed to exhibit the complexity of these states. This complexity will be related to the transition probabilities and the present results compared to studies by other investigators. These results will now permit an analysis of the predissociation behavior of this system.

Brief descriptions of the work completed this year will be given below. Abstracts of the publications will be given in the body of the report.

II. Abstracts of Publications

- a. The $^5\Sigma_g^+$ States of N_2 , M. Krauss and D. B. Neumann, Mol. Phys., to be published.

The electronic structure and energy curves of the $1^5\Sigma_g^+$ and $2^5\Sigma_g^+$ states of N_2 have been analyzed using the multi-configuration self-consistent-field (MC-SCF) method for calculating the wavefunctions and energies. The ab initio model curve for the $1^5\Sigma_g^+$ state obtains an r_e of 1.69Å and a D_e of 825 cm^{-1} . There is also a barrier with a maximum at 2.21Å with a height of about 800 cm^{-1} which is a novel feature of this calculation. The potential supports two bound vibrational levels and

two shape resonances for $J=0$. The calculated curve differs most from the semi-empirical curve of Carroll in having a larger r_e by about 0.14\AA and a well depth smaller by 250 cm^{-1} .

The $^5\Sigma_g^+$ curve is known experimentally to predissociate both the $B^3\Pi_g$ and $a^1\Pi_g$ vibration-rotation levels above the dissociation limit. Conversely, two-body radiative association of two $N(^4S)$ atoms is known to occur through the interaction of the $1^5\Sigma_g^+$ and B and a states. The two-body radiative rates are analyzed in terms of the likely spin-orbit interaction between the $1^5\Sigma_g^+$ and B and a states and the ratio of these rates is calculated under the assumption that the predissociation rate exceeds the radiative in both cases. The ratio of the two-body associative rates k^B/k^a is calculated to be roughly 20 which is to be compared to an experimental ratio of 32.

- b. $^3\Sigma_u^- - ^3\Sigma_u^+$ Coupling in the O_2 $B^3\Sigma_u^-$ Predissociation, P. S. Julienne, J. Mol. Spectrosc., to be published.

The role of $B^3\Sigma_u^- - 2^3\Sigma_u^+$ spin-orbit mixing in the O_2 Schumann-Runge predissociation is investigated. The $2^3\Sigma_u^+$ state is found to cross the $B^3\Sigma_u^-$ state near 2.0\AA with an interaction matrix element of approximately 55 cm^{-1} . This state contributes to the widths of the B $v \geq 6$ levels, but introduces only small level shift perturbations. When the partial widths due to the $^3\Sigma_u^- - ^3\Sigma_u^+$ interaction are added to the previously calculated widths due to the $^5\Pi_u$, $^3\Pi_u$, and $^1\Pi_u$ states, reasonable agreement is obtained with experimental measurements on $O^{16}O^{16}$ and $O^{18}O^{18}$. The possibility of non-Lorentzian line profiles and the dependence of the width on rotational quantum number is investigated. The approximation of the spin-orbit matrix element by its value at the crossing point is shown to be a good approximation for calculating the second difference perturbations.

III. Excited States of N_2

a. Introduction

The production of odd nitrogen in the form of the excited states, $N(^2P)$ or $N(^2D)$, is particularly significant for the production of vibrationally excited $NO(X^2\Pi)$. Zipf^{1/} has emphasized the aeronomic significance of exciting the electric-dipole allowed states of N_2 , the $^1\Pi_u$ and $^1\Sigma_u^+$, which subsequently predissociate. But relatively little has been said about dipole forbidden states that are likely to be either repulsive or predissociated. Since such states tend to be unobserved, they also tend to be ignored except to the extent to which they are required to explain the predissociation of the allowed states. However, electron impact cross sections for exciting these states can be appreciable and they may contribute substantially to the production of excited nitrogen atoms.

The forbidden states of the most interest in this context are the $^3\Pi_u$ states. Dressler^{2/} recognized that the $3\sigma_g n p \pi_u$, $^1\Pi_u$ Rydberg series was predissociated by a triplet state and suggested the continuum of the $^3\Pi_u$ state which is described as either C and C' diabatic states or some appropriate pair of adiabatic $^3\Pi_u$ states. Carroll and Mulliken^{3/} had analyzed this system earlier and found it useful to use the diabatic description since they concluded that the C-C' interaction is relatively weak. The left-hand limb of the C' state is predicted to intersect the $^1\Pi_u$ Rydberg states and predissociate them to the $^4S + ^2D$ asymptote.

Dressler also noted that in contrast to the $^1\Pi$ levels the $^1\Sigma^+$ Rydberg levels do not show strong predissociation. He ascribed this fact to the absence of an excited valence state of species $^3\Sigma_u^+$. But the $^3\Pi_u$

states can also interact by a spin-orbit mechanism with the $1\Sigma_u^+$ states and the weak predissociation can be used to analyze the strength of this mixing.

The present calculations permit a more detailed discussion of these problems in the context of an analysis of the electronic structure of the excited states of N_2 . We will review the current understanding of the electronic states and try to illumine the complex structure with the present calculations. In addition to this reexamination of the electronic structure we will present the analysis of the transition probabilities for exciting these states. The transition probabilities for the $3\Pi_u - 3\Pi_g$ transition will be compared to other theoretical calculations. Previous calculations of the excited states of N_2 have not considered as complete a multi-configurational analysis as has been attempted here and the efficacy of such approximations will be considered here.

b. Valence States of N_2

The adiabatic asymptotic correlations for the nitrogen molecule are given in Table I. Mulliken^{4/} has already catalogued the states of nitrogen and attempted to include many unobserved states predicted by molecular orbital analysis. In this article Mulliken predicted the dominant molecular configuration and asymptotic behavior of many states of N_2 . We will go over the same ground here for a limited set of states of N_2 relevant to the analysis of the dissociation into the lower valence asymptotes of N_2 .

In order to insure formally correct asymptotic behavior for all the valence excited states, all possible occupancies within the chosen set of valence orbitals must be considered with all spin and angular

momentum couplings consonant with a given state symmetry. For example, there are 18 possible $1\Sigma_g^+$ configurations if excitations among $3\sigma_g$, $3\sigma_u$, $1\pi_u$, and $1\pi_g$ are considered. Asymptotically, these orbitals will yield the atomic p orbitals. This total agrees with the 18 possible states that can be constructed for all valence states of nitrogen atom pairs including all possible ionic combinations, i.e., for $p^3 + p^3$, $p^4 + p^2$, $p^5 + p^1$, and $p^6 + p^0$ atomic combinations. The ionic configurations do not represent observed states since none of the negative ion states are bound. Asymptotically, they can be considered as scattering resonances where the penetrating electron has the form of a bound p electron or they can be considered as charge transfer correlating configurations. At finite distances the ion pair states can be quite stable and are to be treated as another class of molecular bound states.

As in the case of $O_2^{5/}$ there is likely a class of bound ion-pair states with equilibrium distances around 2.5\AA . In distinction to the O_2 case excitations from the 2s shell are also significant for N_2 . The excitation energy for the $2s2p^4$, 4P state of N is 10.9 eV while the excitation energy for the $2s2p^5$, 2P states of O lies above the ionization limit at 15.6 eV. The molecular states arising Sp^4 asymptote are also given in Table 1; these states certainly play an important role in the electronic structure of the $^3\Pi_u$ state at shorter distances and in other excited states in that energy region.

Considering just the configurations which span the excitations from the p orbitals, the multi-configuration self-consistent-field (MC-SCF)^{6/} results for the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states show that the major part of the inter-

atomic correlation energy is included. The calculated dissociation energy of the $X^1\Sigma_g^+$ states is about 8.5 eV which is to be compared with an experimental value of 9.7 eV. The absolute error in the calculated dissociation energy for the $A^3\Sigma_u^+$ state is comparable, 2.1 eV calculated vs 3.5 eV experimental. The $^3\Pi_g$ state is calculated to be only 2.0 eV bound but the experimental value is almost 4.8 eV. The main purpose of this study is to determine the transition probabilities to and from the $^3\Pi_u$ states. For this purpose calculations will be done where at least a base MC-SCF wavefunction is available. In the case of the $^3\Pi_u$ states themselves we find that considerably more configurations are required to describe the $1^3\Pi_u$ and $2^3\Pi_u$ states adequately. Since the wavefunction is desired to be most accurate in the region of equilibrium geometry of the X and C states, the base list of configurations was not used for the OVC calculation but was included in the configuration interaction (CI) which followed. For both this CI and for the base OVC calculation on the $B^3\Pi_g$ state we observed long-range barriers in the curves. To what extent there are real barriers in these curves and their magnitude can not be gauged from the present calculations. Even a 92 configuration description is seen to be limited when the entire energy curve is considered.

The calculated energy curves for the $B^3\Pi_g$, $1^3\Pi_u$, and $2^3\Pi_u$ states of N_2 are depicted in Table 2. What are commonly called the C and C' states are both part of the $1^3\Pi_u$ adiabatic curve. The $2^3\Pi_u$ curve at short distances would represent the left-hand limb of the C' diabatic curve and at larger distances would represent part of the asymptotic behavior of the C state. The crossing between C and C' states is reflected in the barrier in the $1^3\Pi_u$ curve at about 1.4 Å and the corresponding minimum in the $2^3\Pi_u$ curve.

The transition probabilities of the (C, C')→B transition reflect this crossing. As seen from Table 2 the $1^3\Pi_u$ transition probability has a zero near 1.4Å due to the crossing; the C state transition probability would be appreciable if we follow the diabatic curve through the crossing. The complexity of these $^3\Pi_u$ states has not been properly described by other theoretical calculations of the $^3\Pi_u$ curves. The "equations-of-motion" method, in particular, is based on a single dominant configuration relative to which excitations are made. For these states there is really no dominant configuration for any considerable range of distance and the energy curves and transition moments of the equation-of-motion method will not go asymptotically correctly and can not represent the adiabatic state quantitatively^{10,11/}.

The most complete analysis of these states has been given by Carroll and Mulliken. They were primarily interested in analyzing the predissociation of the $C^3\Pi_u$ state observed by Büttnebender and Herzberg^{12/}. The predissociation was explained in terms of a bound $^5\Pi_u$ state and this required the subsequent analysis of the $^3\Pi_u$ states in terms of the C and C' states. The $^5\Pi_u$ state was estimated to have an equilibrium distance between 1.4 and 1.5Å. However, preliminary calculations indicate a larger value perhaps even greater than the C' value. Near the equilibrium geometry and to shorter distances the dominant configuration is the $3\sigma_g 1\pi_u^3 1\pi_g^2$ for both the $^5\Pi_u$ and C' states but there is still a significant mixing of this configuration in the C state or the left-hand portion of the $1^3\Pi_u$ state which provides for a one-electron spin-orbit coupling between the $1^3\Pi_u$ and $^5\Pi_u$ states. The calculated $^5\Pi_u$ state has the correct qualitative features predicted by Carroll and Mulliken.

The calculated $1^3\Pi_u$ curve is not sufficiently accurate to provide a quantitative comparison with the predictions of Carroll and Mulliken. The equilibrium geometry of the C state was deduced^{13/} to be 1.15\AA and the calculated curve determines a value of 1.17\AA . There is a barrier near 1.4\AA which is a slightly longer distance than the crossing predicted by Carroll and Mulliken. Whether there is a long-range barrier to the C' or $1^3\Pi_u$ state can not be answered by the present calculation since the calculated curve is about 1 eV too high relative to the asymptote. It should be noted that most base configuration OVC calculations yield asymptotic barriers since no dispersion interactions are included. The absolute error in the $^3\Pi_u$ curve is similar to that found for the X, A, and B states but is more dramatic here since the C well depth is only a little larger than 1 eV.

The $2^3\Pi_u$ state minimum is within 0.5 eV of the $1^3\Pi_u$ maximum. The left-hand limb rises more rapidly than the diabatic C' left-hand limb assumed to predissociate the $1^1\Pi_u$ Rydberg states^{14/}. Again the long range behavior of this adiabatic curve exhibits a number of slope changes and appears to have a long range barrier. Such a barrier if it exists would inhibit dissociation into the $^4S + ^2P$ asymptote.

c. Rydberg States of N_2

The $F^3\Pi_u$ and $G^3\Pi_u$ Rydberg states have been observed by threshold electron impact spectra^{15/}. Leoni and Dressler estimated the $G^3\Pi_u$ as the triplet analog of the $c^1\Pi_u$ state and Ogawa and Tanaka^{16/} suggested the $F^3\Pi_u$ level was in the region of 102600 cm^{-1} on the basis of a Rydberg extrapolation. Joyez et al obtain agreement with the Leoni and Dressler curves if they

rationalize the non-observance of the $v=0$ level of the $F^3\Pi_u$ state by a small Franck-Condon factor for excitation from the ground state. However, this Franck-Condon factor should not be that small and we suggest that the levels are misassigned and that the level at 12.98 eV is, in fact, the $v=0$ of the $F^3\Pi_u$ state.

The calculations we have done of the Rydberg levels would support this reassignment. We have not been able to mix Rydberg configurations directly with valence in an MC-SCF calculation since the effective correlation behavior of the two types of states are very different. Either a very large number of configurations or a non-orthogonal molecular orbital basis is required to adequately represent the correlation to the same level of accuracy in both Rydberg and valence configurations. In order to model this mixing problem we have calculated Rydberg configurations whose energies can then be fixed by the limiting ion energy.

Two ion states are of interest for the analysis of the F and G states and the low-lying predissociating singlet Rydberg states, the $X^2\Sigma_g^+$ and $A^2\Pi_u$. Below 13 eV the only Rydberg states of interest are the:

$(X^2\Sigma_g^+) \text{ core} +$

$3s\sigma_g$ $E^3\Sigma_g^+$, $a'^1\Sigma_g^+$

$3p\sigma_u$ $D^3\Sigma_u^+$, $c'^1\Sigma_u^+$

$3p\pi_u$ $G^3\Pi_u$, $c^1\Pi_u$

$(A^2\Pi_u) \text{ core} +$

$3s\sigma_g$ $F^3\Pi_u$, $o^1\Pi_u$

On the basis of molecular orbital theory and calculations we can expand on the understanding of the experimental diabatic curve energy positions and

the interactions between the Rydberg and valence states. Note that the diabatic notation has been used for the states.

Only a few vibrational levels of the $E^3\Sigma_g^+$ and $a''^1\Sigma_g^+$ curves have been observed. Michels^{17/} has noted that the a'' curve is cut by the left-hand limb of a strongly bound, $2^1\Sigma_g^+$, valence curve that connects asymptotically to the $2D + 2D$ asymptote. The dominant configuration is found to be $3\sigma_g^2 1\pi_u^2 2^1\pi_g^2$ which is also the dominant configurations in the $5\Sigma_g^+$ energy curves^{18/}. There is also a $3\Sigma_g^+$ state which is more repulsive. In the molecular orbital picture the $2^1\Sigma_g^+$ state is very attractive due to the very large off-diagonal mixing between the $3\Sigma^- - 3\Sigma^-$ and $1\Delta^{+2} + 1\Delta^{-2}$ configurations. For both the $3\Sigma_g^+$ and $5\Sigma_g^+$ states there is only one possible coupling.

The valence $3\Sigma_g^+$ curve is apparently too repulsive to predissociate the E state and Michels' curves can imply that the $2^1\Sigma_g^+$ valence curve is the culprit. But there is no first-order spin orbit coupling between the $3\Sigma_g^+$ and $1\Sigma_g^+$ states. However, there is a first order spin-orbit coupling between the $3\Sigma_g^+$ and $5\Sigma_g^+$ states and extrapolating our previously calculated $1^5\Sigma_g^+$ curve would intersect the $E^3\Sigma_g^+$ Rydberg state at about the right energy. It is seen that the predissociation of the E and a'' states then arises from different sources and the similar cut-off structure is a coincidence.

Dressler describes the $1\Sigma_u^+$ absorption spectra as the interaction between a Rydberg $C' 1\Sigma_u^+$ and $b' 1\Sigma_u^+$ valence state. Lefebvre-Brion^{19/} describes the valence state as a mixture of $\pi_u^3 \pi_g$ and $3\sigma_g^2 3\sigma_u$ configurations where the $3\sigma_u$ molecular orbital is valence-like. Although the b' valence state is attractive like the A state, the $2^3\Sigma_u^+$ is very repulsive. Therefore,

we do not expect any homogeneous interactions with the Rydberg $D^3\Sigma_u^+$ state. The $D^3\Sigma_u^+$ Rydberg state is expected to be slightly below the $G^3\Pi_u$ state in energy^{15/}. The C and C' states are very close in energy according to Dressler but our present calculation finds an energy difference of 0.1 eV which agrees with the earlier calculations of Lefebvre-Brion and Moser^{20/}. The electron impact excitation spectrum of the D state has been measured^{21/} and the $v=0$ level at least is not predissociated. The calculated left-hand limb of the C' $^3\Pi_u$ state does not intersect the D or G states near their lower V levels and they should emit like the $v=0$ level of the $C^1\Pi_u$ state. It is a commentary on the deperturbation modelling that the molecular orbital results and deperturbation results predict somewhat different diabatic curves. The D state would be predissociated by rotational-electronic coupling with the C' state.

The G and c states are calculated to be much closer in energy than indicated by the experimental energy separation. Again there is a problem of defining the diabatic states. Again the G state is homogeneously perturbed by the C' and the c state is coupled to the C' by spin-orbit coupling. It should be noted that the c' $^1\Sigma_u^+$ state is also coupled to the C' by spin-orbit coupling and is probably weakly predissociated.

The F and o states are calculated to be separated by 0.09 eV which is about 0.1 eV less than the separation calculated by Lefebvre-Brion and Moser. We assign the level at 12.98 eV to be the $v=0$ of the F state. All of the vibrational levels of the F state should couple to the C' state homogeneously. Joyez et al suggested the lack of observation of the $V=0$ in their assignment was due to an unfavorable Franck-Condon factor. However, the Franck-Condon factors for excitation to $V=0$ and $V=1$ would be comparable

if we compare the transitions to the $A^2\Pi_u$ ion state^{22/}. They should observe the lowest $v=0$ level and we believe they have at 12.98 eV.

The Rydberg levels above these states have been discussed by Mulliken and Ermler^{23/}. Mulliken also notes that a possible cause of predissociation of the $^3\Sigma_g^+$ state of the X family of Rydberg states is the $1^5\Sigma_g^+$ state. We have suggested earlier that this $1^5\Sigma_g^+$ state also predissociates the $E^3\Sigma_g^+$ state with a crossing on its right-hand limb.

The calculation of the coupling of the Rydberg and valence states are still in progress and should be completed shortly.

IV. Meetings

We reviewed the program at a contractor's meeting held in April 1976 at the Air Force Weapons Laboratory, Kirtland AFB. As a result of that meeting we sent the contractor reports of our group and an analysis of our work to Lt. J. Lillis, AF Weapons Lab/DYT.

Table 1

Adiabatic Asymptotic Correlations of Molecular States

$^4S_0 + ^4S_0$	0	$^1\Sigma_g^+; ^3\Sigma_u^+; ^5\Sigma_g^+; ^7\Sigma_u^+$
$^4S + ^2D$	2.4	$^3, ^5\Sigma_{g,u}^+; \Pi_{g,u}; \Delta_{g,u}$
$^4S + ^2P$	3.6	$^3, ^5\Sigma_{g,u}^-; \Pi_{g,u}$
$^2D + ^2D$	4.8	$^1\Sigma_g^+(3); ^1\Sigma_u^-(2); ^1\Pi_g(2); ^1\Pi_u(2); ^1\Delta_g(2); ^1\Delta_u; ^1\phi_g;$ $^1\phi_u; ^1\Gamma_g; ^3\Sigma_u^+(3); ^3\Sigma_g^-(2); ^3\Pi_u(2); ^3\Pi_g(2); ^3\Delta_u(2);$ $^3\Delta_g; ^3\Sigma_u; ^3\sigma_g; ^3\Gamma_u;$
$^2D + ^2P$	6.0	$^1, ^3\Sigma^+; \Sigma^-(2); \Pi(3); \Delta(2); \phi_{g,u}$
$^2P + ^2P$	7.1	$^1\Sigma_g^+(2); ^1\Sigma_u^-; ^1\Pi_g; ^1\Pi_u; ^1\Delta_g; ^3\Sigma_u^+(2); ^3\Sigma_g^+(2); ^3\Sigma_g^-;$ $^3\Pi_g; ^3\Pi_u; ^3\Delta_u$
$N^+(^3P)+N^-(^3P)$	14.5 ?	$^1, ^3\Sigma^+(2); \Sigma^-; \Pi(2); \Delta_{g,u}$
$N^+(^1D)+N^-(^3P)$	16.4 ?	$^3\Sigma^+; \Sigma^-(2); \Pi(3); \Delta(2); \phi_{g,u}$
$N^+(^1S)+N^-(^3P)$	18.5 ?	$^3\Sigma^-, \Pi_{g,u}$
$N^+(^3P)+N^-(^1D)$?	$^3\Sigma^+; \Sigma^-(2); \Pi(3); \Delta(2); \phi_{g,u}$
$N^+(^3P)+N^-(^1S)$?	$^3\Sigma^-, \Pi_{g,u}$
$N^+(^1D)+N^-(^1D)$?	$^1\Sigma^+(3); \Sigma^-(2); \Pi(4); \Delta(3); \phi(2); \Gamma_{g,u}$
$N^+(^1D)+N^-(^1S)$?	$^1\Sigma^+, \Pi, \Delta_{g,u}$
$N^+(^1S)+N(^1D)$?	$^1\Sigma^+, \Pi, \Delta_{g,u}$
$N^+(^1S)+N^-(^1S)$?	$^1\Sigma_{g,u}^+$
$N^{+2}(^2P)+N^{-2}(^2P)$?	$^1, ^3\Sigma^+(2); \Sigma^-; \Pi(2); \Delta_{g,u}$
$N^{+3}(^1S)+N^{-3}(^1S)$?	$^1\Sigma_{g,u}^+$
$N(^4S)+N(^4P, sp^4)$	10.9	$^1, ^3, ^5, ^7\Sigma^+; \Pi_{g,u}$
$N(^4S)+N(^2P, sp^4)$?	$^3, ^5\Sigma^+; \Pi_{g,u}$
$N(^4S)+N(^2D, sp^4)$?	$^3, ^5\Sigma^-; \Pi; \Delta_{g,u}$
$N(^4S)+N(^2S, sp^4)$?	$^3, ^5\Sigma_{g,u}^-$

Table 2

Energies and Transition Moments: N_2 , $1^3\Pi_g$, $1^3\Pi_u$, $2^3\Pi_u$ States

Base Configurations

$R(A^\circ)$	$E_B(1^3\Pi_g)$	$E(1^3\Pi_u)$	$E(2^3\Pi_u)$	$\langle B Z 1^3\Pi_u \rangle$	$\langle B Z 2^3\Pi_u^- \rangle$
	-108.	-108.	-108.		
1.0	.646843	.598583	.256125	-1.0522	0.0992
1.1	.739246	.659816	.431940	-0.9979	0.1198
1.2	.769433	.660941	.528551	-0.8991	0.1473
1.3	.768565	.635377	.582585	-0.7343	0.1976
1.4	.754040	.619280	.600926	0.0460	-0.5206
1.5	.735187	.623852	.590408	0.1723	-0.2859
1.6	.716866	.623279	.575323	0.2147	-0.1559
1.7	.701567	.620983	.565119	0.2211	-0.0919
1.9	.684154	.624067	.545191	0.1718	-0.0614
N_2 (1), (2) $3^3\Pi_u$ States					
92 configurations (chosen from 128)					
$R(A^\circ)$	$E(1^3\Pi_u)$	$E(2^3\Pi_u)$			
	-108.	-108.			
1.0	.614932	.279956			
1.1	.679323	.456059			
1.2	.682895	.552526			
1.3	.659234	.605391			
1.4	.648987	.640821			
1.5	.659414	.639423			
1.6	.662556	.634914			
1.7	.662934	.628008			
1.9	.666630	.611353			

Energy and transition moment in atomic units:

Energy 1 a.u. = 27.21 eV

Transition moment 1 a.u. = 2.54 Delyes

References

1. E. C. Zipf, Abstr. 55th Annual Am. Geophys. Union Meeting, Trans. Am. Geophys. Union 55, 363 (1974).
2. K. Dressler, Can. J. Phys. 47, 547 (1969).
3. P. K. Carroll and R. S. Mulliken, J. Chem. Phys. 43, 2170 (1965).
4. R. S. Mulliken, "The threshold of space," (Pergamon Press, Ltd., New York), 1956, p. 169.
5. M. Krauss and D. Neumann, J. Chem. Phys. 63, 5073 (1975).
6. G. Das and A. C. Wahl, "BISON-MC: A Fortran Computing System for Multiconfiguration Self-Consistent-Field (MC-SCF) Calculation on Atoms, Diatoms, and Polyatoms," Argonne National Laboratory Report ANL-7955 (1972).
7. H. F. Schaefer III and W. H. Miller, J. Chem. Phys. 55, 4107 (1971).
8. P. S. Julienne and M. Krauss, J. Mol. Spectrosc. 56, 270 (1975).
9. P. S. Julienne, D. Neumann and M. Krauss, J. Chem. Phys. 64, 2990 (1976).
10. J. Rose, T. Shibuya, and V. McKoy, J. Chem. Phys. 58, 2699 (1973).
11. D. L. Yeager and V. McKoy,
12. G. Büttenbender and G. Herzberg, Ann. Phys. 21, 577 (1935).
13. J. T. Vanderslice, E. A. Mason and E. R. Lippincott, J. Chem. Phys. 30, 129 (1959).
14. M. W. Leoni, "Die Kerndynamik in dengekoppelten Elektronenzuständen des N₂-Moleküls," Thesis Federal Institute of Technology, Switzerland, 1972; M. W. Leoni and K. Dressler, J. Appl. Mathematics and Physics ZAMP 22, 794 (1971).
15. J. Mazeau, R. I. Hall, G. Joyez, M. Landau, and R. Reinhardt, J. Phys. B6, 873 (1973); G. Joyez, R. I. Hall, J. Reinhardt, and J. Mazeau, J. Electron Spectrosc. Relat. Phenom. 2, 183 (1973).
16. M. Ogawa and Y. Tanaka, Can. J. Phys. 40, 1593 (1962).
17. H. H. Michels, J. Chem. Phys. 53, 841 (1970).

18. M. Krauss and D. Neumann, Mol. Phys., to be published.
19. H. Lefebvre-Brion, Can. J. Phys. 47, 541 (1969); R. S. Mulliken, Chem. Phys. Lett. 25, 305 (1974).
20. H. Lefebvre-Brion and C. M. Moser, J. Chem. Phys. 43, 1394 (1965).
21. R. S. Freund, J. Chem. Phys. 54, 1407 (1971).
22. D. C. Jain and R. C. Sahni, Int. J. Quantum Chem. 2, 325 (1968).
23. R. S. Mulliken, J. Mol. Spectrosc. 61, 92 (1976); W. C. Ermler and R. S. Mulliken, J. Mol. Spectrosc. 61, 100 (1976).

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