MULTIPHOTON SPECTROSCOPY OF RYDBERG STATES
OF SMALL MOLECULES*
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INTRODUCTION

Multiphoton ionization techniques provide a versatile means for studying highly excited states of atoms and molecules and provide a valuable complement to traditional techniques based on single-photon absorption and ionization studies. In this paper we present the results of new multiphoton ionization studies of molecular nitrogen and molecular oxygen that serve to illustrate the power of these techniques.

AUTOIONIZING STATES OF N2

Figure 1 shows the single-photon ionization spectrum of N2 in the region near the X 2Σg+, ν = 0 ionization threshold, taken at a wavelength resolution of 2.5 cm⁻¹ and a temperature of 78K.¹ In this region, only the weak transitions to the (X 2Σg+, nπσ, 7) Rydberg complexes converging to the ν = 1 threshold have been assigned unambiguously;²⁻³ these are indicated in the figure.

Although there have been many attempts to assign the two intense bands centered at 126280 and 126400 cm⁻¹, no definitive assignments have been made to date.⁴⁻⁵ The

*This work was supported in part by the U.S. Department of Energy, Assistant Secretary for Energy Research, Office of Health and Environmental Research, under Contract W-31-109-Eng-38. E. F. McCormack was supported by an appointment to the Alexander Hollaender Distinguished Postdoctoral Fellowship Program sponsored by the U.S. Department of Energy, Office of Health and Environmental Research, and administered by Oak Ridge Associated Universities.

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failure to assign the intense bands in this region results from an inability to resolve rotational structure in the single-photon spectrum and from the poor correlation of the quantum defects of these features with those in other spectral regions. Although a new high-resolution, single-photon absorption spectrum of jet-cooled N\textsubscript{2} provides considerable information on the bands in this region, the spectral widths of the features within many of the bands converging to the A \textsuperscript{2}\Pi\textsubscript{u} and B \textsuperscript{2}\Sigma\textsuperscript{+}\textsubscript{u} states of N\textsubscript{2}\textsuperscript{+} make their analysis difficult or impossible.

Double-resonance spectroscopy offers an alternative to single-photon techniques and can often overcome the difficulties associated with spectral congestion. Recently, we have performed a double-resonance study of the energy region of Figure 1 by using one laser to pump individual rotational lines of the two-photon a \textsuperscript{1}\Pi\textsubscript{g}, v = 5 \leftrightarrow X \textsuperscript{1}\Sigma\textsuperscript{+}\textsubscript{g}, v'' = 0
transition and by monitoring the mass-selected ionization signal obtained by using a second laser to probe transitions from these levels to the energy region of Figure 1. The overall three-photon transition accesses the same parity levels as the single-photon transitions, but because the probe transition is excited from a single rotational level, the observation of resolved rotational structure is possible even for severely broadened lines.

Because of the one-photon parity selection rule $+ \leftrightarrow -$, the allowed rotational branches in transitions excited from a selected a $^1\Pi_g$, $v' = 5$, $J'$ level will depend both on the pump transition to the a $^1\Pi_g$ state and on the symmetry of the final state. Pump transitions via O, Q, and S branches populate the $\Lambda^+$ component of the a $^1\Pi_g$ state, while those via P and R branches populate the $\Lambda^-$ component. It is straightforward to determine that only P and R branches will be excited in $^1\Sigma_u^+ \leftarrow a^1\Pi_g^+$ probe transitions, while only Q branches will be excited in $^1\Sigma_u^+ \leftarrow a^1\Pi_g^+$ probe transitions. The P, Q, and R branches will all be excited in $^1\Pi_u$ or $^1\Delta_u \leftarrow a^1\Pi_g$ probe transitions, since each rotational level of a $\Pi$ or a $\Delta$ state has both $+$ and $-$ parity levels. Thus, a comparison of the observed branches from different levels of the a $^1\Pi_g$, $v' = 5$ state helps to determine the symmetry of the final autoionizing states. In addition to the pattern of branches excited from the different levels of the a $^1\Pi_g$ state, the observation of low-lying rotational levels of the final autoionizing states also aids in the symmetry determination; $^1\Pi$ states will be missing $J = 0$ levels, and $^1\Delta$ states will be missing $J = 0$ and 1 levels.

Figure 2 shows a representative double-resonance ionization spectrum in the energy region of the diffuse bands in Figure 1, excited via the P(4) pump transition. The discussion below is limited to the region between 126200 and 126400 cm$^{-1}$. Spectra recorded for a number of different pump transitions indicate that probe transitions to four different electronic states are observed in this region. In addition, the observation of only Q-branch probe transitions for P and R pump transitions and of only P- and R-branch transitions for S and Q pump transitions indicates that all four electronic states are $^1\Sigma_u^+$ states. The assignment of the electronic states responsible for the three sharp features in this region of Figure 2 is based on the term energies and rotational constants determined
Figure 2. The (2+1') ionization spectrum via the P(4) pump transition in a small region of the spectrum. The energy is referenced to X \(^1\Sigma_u^+\), \(v'' = 0, J'' = 0\).

from the spectra.\(^9\) The three states correspond to the \(b' \ ^1\Sigma_u^+\), \(v' = 42\) and 43 valence levels and the \((X \ ^2\Sigma_g^+)\rho \pi \ ^1\Sigma_u^+, \ v' = 1\) Rydberg state, as is indicated in Figure 2.

The assignment of the broad feature is less straightforward.\(^9\) This feature must correspond to a Rydberg state converging to the \(A ^2\Pi_u\) or \(B ^1\Sigma_u^+\) state of the ion, and the only possible electronic configurations are therefore \((A ^2\Pi_u)\Sigma\pi \ ^1\Sigma_u^+\) and \((B ^2\Sigma_u^+)\Sigma\sigma \ ^1\Sigma_u^+\). In order to choose between these and to assign the \(n\) and \(v\) values, it is necessary to use other information such as quantum defects, term energies, rotational constants, and Franck-Condon factors. For both possible electron configurations, the only value of principal quantum number that provides a reasonable quantum defect is \(n = 3\).\(^10\) The assignment of the vibrational quantum number is somewhat more difficult, but considerable information is provided from observed transition intensities. In particular, the single-
photon ionization spectrum\textsuperscript{1} shows that the band under consideration is very intense in the spectrum excited from $X \, ^1\Sigma_g^+$, $v'' = 0$ but is absent in the spectrum excited from $X \, ^1\Sigma_g^+$, $v'' = 1$. The Franck-Condon factors\textsuperscript{11} for excitation from $X \, ^1\Sigma_g^+$, $v'' = 0$ and 1 show that the only vibrational levels consistent with this observation are $(A \, ^2\Pi_u) \, ^3\Sigma_u^+, v = 1$ or 2 and $(B \, ^2\Sigma_u^+) \, ^3\sigma \, ^1\Sigma_u^+, v = 0$. Furthermore, the very small Franck-Condon factor (0.008)\textsuperscript{11} for the $(A \, ^2\Pi_u) \, ^3\Sigma_u^+, v = 1 \leftrightarrow ^1\Pi_g$, $v' = 5$ transition almost certainly eliminates $(A \, ^2\Pi_u) \, ^3\Sigma_u^+, v = 2$ (which yields $n^* = 3.00$ and $\delta = 0.00$) and $(B \, ^2\Sigma_u^+) \, ^3\sigma \, ^1\Sigma_u^+, v = 0$ (which yields $n^* = 2.10$ and $\delta = 0.90$). The resulting quantum defects are both reasonable.

We have chosen to assign the band in question as $(B \, ^2\Sigma_u^+) \, ^3\sigma \, ^1\Sigma_u^+, v = 0$ for two reasons. First, the assignment of $(B \, ^2\Sigma_u^+) \, ^3\sigma \, ^1\Sigma_u^+, v = 0$ to the band at 126269.5 cm\textsuperscript{-1} is consistent with the assignment by Helm and Cosby\textsuperscript{12} of $(B \, ^2\Sigma_u^+) \, ^3\Sigma^+ 1\Sigma_u^+, v = 1$ to a triplet band at 126910 cm\textsuperscript{-1}. The experimental singlet-triplet splitting [obtained by assuming that the $(B \, ^2\Sigma_u^+) \, ^3\sigma, v = 0$ - 1 splitting is identical to that of the ionic convergence limit] is then 1730 cm\textsuperscript{-1}, which is in reasonable agreement with the calculated value\textsuperscript{13} of 2190 cm\textsuperscript{-1}. Second, Roncin et al.\textsuperscript{14} have recently assigned the $(A \, ^2\Pi_u) \, ^3\Sigma_u^+, v = 0$ level to a weak band at 123309 cm\textsuperscript{-1}; the separation between this band and the band under consideration is 2960.5 cm\textsuperscript{-1}, which does not agree well with the $A \, ^2\Pi_u$, $v^+ = 0$ - 2 splitting\textsuperscript{15} of 3716.8 cm\textsuperscript{-1}. Although Carroll and Hagim\textsuperscript{16} have assigned a band at 124299 cm\textsuperscript{-1} in the single-photon absorption spectrum to the $(B \, ^2\Sigma_u^+) \, ^3\sigma \, ^1\Sigma_u^+, v' = 0$ level, this assignment has been questioned by Huber and Jungen,\textsuperscript{7} and the present assignment appears to be more consistent with our double-resonance results.

The present double-resonance studies have allowed the assignments of a number of other previously unidentified bands in the region between the $N_2^+ X \, ^2\Sigma_g^+$, $v^+ = 0$ and 1 thresholds. We are currently extending these studies to both lower and higher energies and to include different intermediate vibrational levels in the $a \, ^1\Pi_g$ state.
TWO-PHOTON SPECTROSCOPY OF O₂

In recent years, two-photon spectroscopy of O₂ has provided a significant amount of new information on the single-photon, forbidden, gerade Ryberg states converging to the X 2Π ground state of O₂⁺.¹⁷-²⁷ These experiments are important because very little information exists on the Rydberg series converging to the O₂⁺ ground state and because there are few detailed studies of the rotational structure of Rydberg series converging to ionic states with Π symmetry. The earliest work focused on two-photon spectroscopy of the (X 2Πg)3sΠg, 1,3Πg states,¹⁷-²² but more recently Park et al.²³-²⁶ and Ogorzalek Loo et al.²⁷ have obtained two-photon resonant, three-photon (2+1) ionization spectra of the (X 2Πg)3d,4s and (X 2Πg)4d,5s complexes from both the X 3Σg⁻ and a 1Δg levels. In contrast to the strongly predissociated structure of the (X 2Πg)3sΠg bands, the (X 2Πg)3d,4s and 4d,5s bands display sharp rotational structure, at least for the lowest rotational levels within each band. The assignment of these spectra was not straightforward because of the large number of electronic states arising from the coupling of an nd electron with the O₂⁺ X 2Πg ion core and because of the large spin-orbit interaction that mixes singlet and triplet levels. However, the comparison of spectra obtained from the different electronic states has allowed the rotational analysis and assignment of a number of bands.

We have recently obtained (2+1) ionization spectra of ground state O₂ in the two-photon energy region beginning at the 4d-5s complex (~91000 cm⁻¹) and extending to the O₂⁺ X 2Π₁/₂g, v⁺ = 0 ionization threshold.²⁸ For n ≥ 5, only a few rotational lines are observed for each band, and the electronic state assignments are not definitive. However, two Rydberg series are observed for n = 4 - 9, v' = 0, and one can be tentatively assigned as the ndπ 1Σ⁺ g, v' = 0 series. The n = 3 member of this series was analyzed by Ogorzalek Loo et al.²⁷ and Park et al.²⁵ An analogous pair of Rydberg series is observed for n = 5 - 7, v' = 1. These v' = 1 series have been extended above the X 2Π₁/₂g, v⁺ = 0 threshold by recording the direct two-photon ionization spectrum. There, Rydberg states with n = 8 - 12, v' = 1 that decay by vibrational autoionization into the X 2Πg, v⁺ = 0 ionization continuum have been identified.
A representative example of the (2+1) ionization spectrum of O\textsubscript{2} \((^3\Sigma_g^-)\), \(v'' = 0\) is shown in Figure 3. This energy region is expected to include the 5d,6s, \(v' = 1\) complex as well as the 7d,8s, \(v' = 0\) complex, and the resulting spectral pattern is typical of that seen for successive Rydberg complexes in the entire region between 94900 \(\text{cm}^{-1}\) and the ionization threshold. The lowest energy band in Figure 3 corresponds to the W1 band of Park et al.,\textsuperscript{23} which was assigned as a transition to an \(n = 5, v' = 1\) Rydberg state. A second band that was not observed by Park et al.\textsuperscript{23} is found at 95133.7 \(\text{cm}^{-1}\). The 219.7 \(\text{cm}^{-1}\) splitting is approximately equal to the O\textsuperscript{5+} \((^2\Pi_{1/2g}) - ^2\Pi_{3/2g}\) spin-orbit splitting, which is 199.68 \(\text{cm}^{-1}\) for \(v^+ = 1\).\textsuperscript{29} This finding suggests that both bands are members of the 6s-5d, \(v' = 1\) complex and that the Rydberg states are built on \(^2\Pi_{1/2g}, v^+ = 1\) and \(^2\Pi_{3/2g}, v^+ = 1\) ion cores, respectively. A second pair of bands is observed in Figure 3 at 95154.8 and 95355.7 \(\text{cm}^{-1}\). The 95154.8 \(\text{cm}^{-1}\) band is overlapped by the rotational structure of the 95133.7 \(\text{cm}^{-1}\) band, but consideration of the intensities and rotational structure leads to its identification. These bands are assigned as transitions to the O\textsuperscript{5+} \((^2\Pi_{1/2g})\) and

**Figure 3.** The (2+1) ionization spectrum of O\textsubscript{2} between 94880 and 95400 \(\text{cm}^{-1}\). The spectrum was obtained by monitoring the O\textsuperscript{5+} ion signal.
X $^2\Pi_{3/2g}$ components of the 7d,8s, $v' = 0$ complex; their appearance is similar to that of the 5d,6s bands, but the splitting of 200.9 cm$^{-1}$ between the O$_2^+$ X $^2\Pi_{1/2g}$ and X $^2\Pi_{3/2g}$ components is much closer to the ionic value (200.33 cm$^{-1}$ for $v^+ = 0$) than the splitting observed for the 5d,6s, $v' = 0$ complex (218.6 cm$^{-1}$), indicating a more complete uncoupling of the Rydberg electron from the ion core, as expected. The relatively simple appearances of the bands in Figure 3 and at higher energies as compared to the 3d,4s and 4d,5s complexes, and the clear correlation of the higher energy levels with particular O$_2^+$ ion core states suggests the evolution of the Hund's case (a) and (b) states observed at lower $n$ into the Hund's case (d) or (e) states expected at higher $n$.

Although the qualitative analysis of the O$_2$ spectra is straightforward, the detailed assignments and rotational analyses are still missing. One difficulty with these analyses is that only a few rotational lines are observed for each band. Presumably, a heterogeneous predissociation mechanism is responsible for the absence of higher rotational levels in the present spectra. If this is the case, two-color experiments could provide information on these predissociated levels. In this approach, one laser would be used to scan through the wavelength region of interest, and a second laser would be used to resonantly ionize the oxygen atoms produced by predissociation. By monitoring the O$^+$ ion signal, it may be possible to map out the structure of the higher rotational levels and improve the likelihood of a successful rotational analysis. Multiphoton detection techniques for O $^3P_{0,1,2}$ already exist, and we are currently developing techniques for the detection of O $^1D_2$.

REFERENCES


10. Values of $n^*$ and $\delta$ were calculated from the relations $E_n = E_{\infty} - 109735.166 \text{ cm}^{-1}/(n^*)^2$ and $\delta = n - n^*$.

11. Franck-Condon factors were calculated by using Morse potentials determined from the molecular constants given in K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules (Van Nostrand Reinhold, New York, 1979).


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