

Characterization of Triplet States in Doubly Charged Positive Ions: Assignment of the ${}^3\Pi_g \leftarrow {}^3\Sigma_u^+$ Electronic Transition in N_2^{2+}

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The first direct spectroscopic evidence and characterization of triplet states in a molecular dication is reported. The ${}^3\Pi_g \leftarrow {}^3\Sigma_u^+$ electronic absorption between excited states of N_2^{2+} is recorded by ion-laser coaxial beam photofragmentation spectroscopy. Over 300 rotational lines are resolved, and 13 parameters characterizing the upper and lower electronic states are determined. The results are compared with calculated potential energy curves. Dissociation lifetimes of the upper rotational levels are measured, and possible mechanisms of dissociation are discussed.

Introduction

Molecular dications are unique chemical species whose properties are presently being investigated by both experimentalists¹⁻⁶ and theorists.⁶⁻¹¹ Effort is also being made to determine the feasibility of using molecular dications as energy storage systems. The stability of molecular dications was first predicted by Pauling,¹² who suggested that even the two-electron diatomic He_2^{2+} could be quasibound, due to the fact that the bonding interaction can overcome the electrostatic repulsion at small internuclear distances. Although molecular dications have been observed in mass spectrometers^{13,14} since the 1930s and many studies have elucidated electronic properties (appearance potentials¹⁵ and excited electronic state energies¹⁶⁻¹⁹), the details of other properties such as chemical bonding are not well characterized. The lack of experimental information on chemical bonding, structure, and dynamics can be attributed, in part, to low number densities of dications and extremely high reactivity to charge transfer.

Despite these difficulties, the optical emission spectra of a few diatomic dications have been recorded and several singlet states have been characterized. The first spectroscopic evidence to support the existence of stable excited electronic states was the rotationally resolved spectra reported for N_2^{2+} in 1958 by Carroll,²⁰ and more recently confirmed and analyzed by Cossart et al.²¹ In both of these experiments, the emission spectrum recorded at 158.9 nm following the formation of N_2^{2+} in an electric discharge was assigned to the $D^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transition. Several emission spectroscopic studies on NO in an electric discharge have also been reported.²²⁻²⁴ Broad emission observed at 317.0 nm has been ascribed²² to the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition in NO^{2+} . Subsequently, a rotationally resolved optical emission spectrum²³ has been obtained at 256.3 nm for NO in a low-pressure electric discharge. By use of this spectrum in conjunction with data from photoion-fluorescence photon coincidence,²² translational energy loss spectroscopy,¹⁸ and ab initio calculation,^{7,9,25} the band was also assigned to the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition in NO^{2+} , contradicting the previous report.²² This ambiguity emphasizes the desirability of mass selection in spectroscopic studies. Despite this ambiguity, emission experiments have proven invaluable to locate the positions and to determine the character of the electronic states involved in the transitions of molecular dications. With excitation spectroscopies, such as photofragment spectroscopy, however, higher sensitivity and spectral resolution can be achieved.

The advantages of using ion-laser coaxial beam photofragmentation spectroscopy to characterize molecular dications has been demonstrated²⁶ for N_2^{2+} , for which the spectrum has been recorded in the region 14 900–19 500 cm^{-1} . This investigation revealed several vibronic bands associated with the ${}^1\Pi_u \leftarrow X^1\Sigma_g^+$ absorption. The vibronic band at 18 300 cm^{-1} has recently been

reexamined through high-resolution studies²⁷ of both ${}^{14}N_2^{2+}$ and ${}^{15}N_2^{2+}$, from which the vibrational numbering of the ${}^1\Pi_u$ state has now been unambiguously determined. Triplet states were not identified despite their expectation from theoretical predictions.^{7,8,10,28} Because N_2^{2+} is isoelectronic with C_2 , one might expect low-energy triplet-triplet transitions.²⁹ Cosby et al. did report two absorption bands²⁶ at $\sim 15\,300$ and $\sim 16\,400$ cm^{-1} , although no assignments were given. In this Letter, we report the first direct spectroscopic observation and characterization of triplet electronic states of a molecular dication. We have examined the previously observed²⁶ 15 300- cm^{-1} band by ion-laser coaxial beam photofragmentation spectroscopy and assigned this band

- (1) Lezius, M.; Märk, T. D. *Chem. Phys. Lett.* **1989**, *155*, 496.
- (2) Curtis, J. M.; Brenton, A. G.; Beynon, J. H.; Boyd, R. K. *Chem. Phys.* **1987**, *117*, 325.
- (3) Saunders, W. A.; Fedrigo, S. *Chem. Phys. Lett.* **1989**, *156*, 14.
- (4) Coolbaugh, M. T.; Peifer, W. R.; Garvey, J. F. *Chem. Phys. Lett.* **1989**, *156*, 19.
- (5) Leach, S.; Eland, J. H. D.; Price, S. D. *J. Phys. Chem.* **1989**, *93*, 7575.
- (6) Olsson, B. J.; Kindvall, G.; Larsson, M. *J. Chem. Phys.* **1988**, *88*, 7501.
- (7) Hurley, A. C. *J. Mol. Spectrosc.* **1962**, *9*, 18.
- (8) Wetmore, R. W.; Boyd, R. K. *J. Phys. Chem.* **1986**, *90*, 5540.
- (9) Cooper, D. *Chem. Phys. Lett.* **1986**, *132*, 377.
- (10) Taylor, P. R.; Partridge, H. *J. Phys. Chem.* **1987**, *91*, 6148.
- (11) Senekowitsch, J.; O'Neil, S. V.; Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1990**, *93*, 562.
- (12) Pauling, L. *J. Chem. Phys.* **1933**, *1*, 56.
- (13) Friedlander, E.; Kallman, H.; Laserfeld, W.; Rosen, B. *Z. Phys.* **1932**, *76*, 60.
- (14) Tate, J. T.; Smith, P. T.; Vaughan, A. L. *Phys. Rev.* **1935**, *48*, 525.
- (15) Märk, T. D.; Hille, E. *J. Chem. Phys.* **1978**, *69*, 2492.
- (16) Rogers, S. A.; Miller, P. J.; Leone, S. R.; Brehm, B. *Int. J. Mass Spectrom. Ion Processes*, in press.
- (17) Appell, J.; Durup, J.; Fehsenfeld, F. C.; Fournier, P. *J. Phys. B* **1973**, *6*, 197.
- (18) O'Keefe, A.; Illies, A. J.; Gilbert, J. R.; Bowers, M. T. *Chem. Phys.* **1983**, *82*, 471.
- (19) Hamdan, M.; Brenton, A. G. *Chem. Phys. Lett.* **1989**, *155*, 321.
- (20) Carroll, P. K. *Can. J. Phys.* **1958**, *36*, 1585.
- (21) Cossart, D.; Launay, F.; Robbe, J. M.; Gandara, G. *J. Mol. Spectrosc.* **1985**, *113*, 142.
- (22) Besnard, M. J.; Hellner, L.; Malinovich, Y.; Dujardin, G. *J. Chem. Phys.* **1986**, *85*, 1316.
- (23) Cossart, D.; Bonneau, M.; Robbe, J. M. *J. Mol. Spectrosc.* **1987**, *125*, 413.
- (24) Besnard, M. J.; Hellner, L.; Dujardin, G. *J. Chem. Phys.* **1988**, *89*, 6554.
- (25) Thulstrup, P. W.; Thulstrup, E. W.; Anderson, A.; Öhrn, Y. *J. Chem. Phys.* **1974**, *60*, 3975.
- (26) Cosby, P. C.; Möller, R.; Helm, H. *Phys. Rev. A* **1983**, *28*, 766.
- (27) Masters, T. E.; Sarre, P. J. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 2005.
- (28) Senekowitsch, J.; O'Neil, S. V.; Knowles, P.; Werner, H.-J. *J. Phys. Chem.*, following paper in this issue.
- (29) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

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to be part of a ${}^3\Pi_g \leftarrow {}^3\Sigma_u^+$ transition. The lower state of this transition, ${}^3\Sigma_u^+$, lies ~ 1.57 eV above the ground ${}^1\Sigma_g^+$ state.²⁸ The upper state is weakly bound, with a calculated well depth of 1370 cm^{-1} , which could support up to two vibrational levels.²⁸ For this transition, greater than 300 lines and 26 out of 27 possible branches have been assigned. From the assignment, 13 parameters characterizing the two electronic states have been determined. Information is obtained about the triplet potential energy curves and the interaction of the electron spin with other angular momenta of the dication. The predissociation lifetimes of the individual rotational states of the upper electronic state are extracted from the sub-Doppler spectral line widths.

Experimental Section

The experimental apparatus is a negative ion-laser coaxial beam photodetachment spectrometer³⁰ which has been extensively modified for dication photofragmentation studies. Modifications to the instrument include the addition of an ion source for dication production, reversal of polarities for positive ion transmission, construction of a photofragment ion separation region, and coincidence detection of the photoproducts. A detailed description of the apparatus and modifications will be published.³¹ Briefly, the dications are formed via 120-eV electron impact on an effusive N_2 beam and extracted into a 90° magnetic sector which selects a particular m/z (mass-to-charge ratio) species. The $m/z = 14$ ion beam, which contains both N_2^{2+} and N^+ , is accelerated by a 2.3-kV potential and coaxially combined, via a merging quadrupole deflector, with the laser beam in a 30-cm interaction region. A kinetic energy release of several electronvolts (typical of molecular dications) resulting from the photodissociation amplifies to an energy dispersion in the laboratory frame of a few hundred electronvolts. Thus, the N^+ photoproducts can be distinguished from the N^+ ions formed in the ion source. The forward and backward scattered photoproducts are separated from the main ion beam in a demerging quadrupole deflector, which also serves as an electrostatic energy analyzer. The three beams (N^+ forward fragment, N^+ backward fragment, and unreacted N_2^{2+} and N^+) then enter a retarding field and travel an additional 40 cm to enhance spatial dispersion. The two N^+ photofragments are collected by two microchannel plate ion multipliers, using coincidence detection in order to discriminate against scattered ions from the main ion beam.

The output of a home-built linear CW dye laser (DCM dye, 700 mW) pumped by an Argon ion laser (7 W) is passed through the interaction region of the ion beam apparatus. The frequency is selected and tuned by a three-plate birefringent filter and a solid etalon. In this configuration, the overall instrumental resolution is 1–2 GHz, resulting from the convolution of the laser line width (1–2 GHz), the angular divergence of the ion and laser beams (0.6 MHz),³⁰ and the energy spread in the ion source (<0.3 GHz). Thus, rotational-state lifetimes of 80 ps or shorter can be measured. The spectra are recorded in 6-cm^{-1} increments, the free spectral range of the etalon. For accurate lifetime measurements, the dye laser is converted into a single-mode ring laser (250 mW, 10-MHz line width) with the addition of a unidirectional device and a scanning thick etalon and galvo plate. The resolution of the lifetime measurements is now limited by the energy spread in the ion source, with the consequence that lifetimes of 500 ps or less can be measured. For both laser configurations, the longitudinal mode structure is monitored with a Fabry-Perot etalon and the wavelength is measured with a traveling Michelson interferometer wavemeter.³² The $m/z = 14$ ion beam current is typically 150 pA, of which 5–10% is estimated from electron impact cross-section measurements^{33,34} to be the molecular dication, N_2^{2+} . The

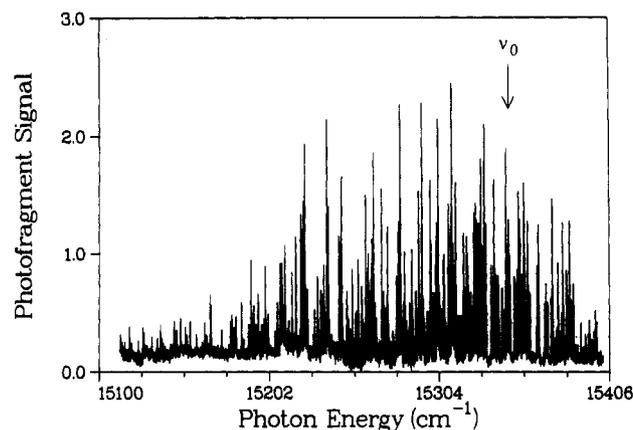


Figure 1. Photofragmentation spectrum of N_2^{2+} in the region 15 100–15 400 cm^{-1} . The spectrum consists of over 300 lines and is assigned to the ${}^3\Pi_g - {}^3\Sigma_u^+$ (0,0) transition. The coincidence ion signal of the photoproducts is recorded as a function of the laser frequency. The band origin, $\nu_0 (=T_{0,0})$, at 15 345.933 cm^{-1} is labeled.

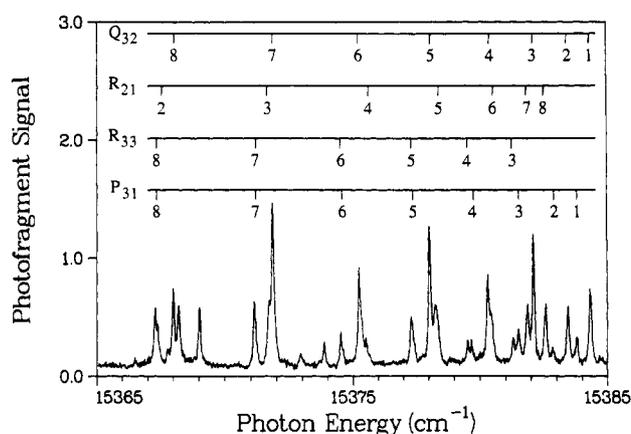


Figure 2. Expanded region of the N_2^{2+} photofragmentation spectrum from 15 365 to 15 385 cm^{-1} . Each of the lines corresponds to an individual ro-vibronic ${}^3\Pi_g - {}^3\Sigma_u^+$ (0,0) transition. Four progressions are each labeled with a letter which denotes ΔJ (e.g., Q implies $\Delta J = 0$) and with subscripts which indicate the upper state spin-orbit and the lower state spin-spin components, respectively. The lower state N'' quantum number is labeled above each line. The line widths are ~ 0.1 cm^{-1} corresponding to lifetimes of the upper ro-vibronic levels of 50 ps.

coincidence signal due to spontaneous dissociation of the dication in the coaxial interaction region is ca. 200 Hz, while the laser-induced coincidence signal is ca. 1.5 kHz for the largest peaks in the photofragmentation spectrum. The latter signal is normalized to the total ion current and the laser power.

Results and Discussion

The photofragmentation spectrum of the 15 300- cm^{-1} band is shown in Figure 1. The complexity of the spectrum strongly suggests that the transition involves states of higher spin multiplicity than the singlet-singlet transitions of N_2^{2+} identified previously.²⁶ Elaborate ab initio calculations²⁸ of the low-energy triplet states by Senekowitsch and O'Neil suggested two possible electric dipole allowed transitions, ${}^3\Pi_g \leftarrow {}^3\Sigma_u^+$ and ${}^3\Sigma_g^- \leftarrow {}^3\Pi_u$, with energies comparable to that observed in this work. Guided by these predictions, we carried out the detailed spectroscopic analysis outlined below; this analysis showed that the 15 300- cm^{-1} band is part of the ${}^3\Pi_g \leftarrow {}^3\Sigma_u^+$ transition. This assignment is consistent with recent kinetic energy release (KER) measurements.³⁵

The observed ${}^3\Pi_g \leftarrow {}^3\Sigma_u^+$ band is made up of more than 300 resolved ro-vibronic lines and spans a spectral region of ca. 300 cm^{-1} . The line widths in the photofragmentation spectrum are inversely proportional to the lifetimes of the ro-vibronic levels in

(30) Hefter, U.; Mead, R. D.; Schulz, P. A.; Lineberger, W. C. *Phys. Rev. A* **1983**, *28*, 1429.

(31) Mullin, A. S.; Szaflarski, D. M.; Yokoyama, K.; Gerber, G.; Lineberger, W. C. *J. Chem. Phys.*, to be published.

(32) Hall, J. L.; Lee, S. A. *Appl. Phys. Lett.* **1976**, *29*, 367.

(33) Märk, T. D. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *45*, 125.

(34) Halas, S.; Adamczyk, B. *Int. J. Mass Spectrom. Ion Phys.* **1972**, *10*, 157.

(35) M. Larsson and co-workers, unpublished results, 1990.

TABLE I: Spectroscopic Constants for $^{14}\text{N}_2^{2+}$ Derived in the Present Work^a

	$^3\Sigma_u^+$	$^3\Pi_g$
$T_{0,0}$	a^b	$a + 15345.933$ (5)
r_0 , Å	1.09406 (8)	1.2078 (1)
B_0	2.0110 (3)	1.6502 (3)
D_0 ($\times 10^6$)	3.0 (10)	3.7 (9)
λ	-0.664 (4)	0.372 (3)
γ ($\times 10^3$)	-1.5 (5)	11.9 (7)
A		-35.286 (5)
p ($\times 10^3$)		2.4 (7)
q ($\times 10^4$)		-3 (1)
o		1.187 (4)

^aAll numbers are in cm^{-1} unless noted. The quoted uncertainties in parentheses are one standard deviation in the last digit. ^bThe term energy of the $^3\Sigma_u^+$ state, a , is determined from theoretical calculations²⁸ to be $\sim 12660 \text{ cm}^{-1}$ (1.57 eV), consistent with KER measurements.³⁵

the upper electronic state. Spectral analysis refinement eventually led to the identification of 333 transitions. Of the 27 possible branches expected for such a triplet-triplet electronic transition, 26 were intense enough to be identified and assigned. Figure 2 displays an expanded view of the 15 365–15 385- cm^{-1} portion of the excitation photofragmentation spectrum. Each of the lines corresponds to an individual ro-vibronic $^3\Pi_g - ^3\Sigma_u^+$ (0,0) transition. Members of four branches that contribute to this transition are labeled. The capital letters denote ΔJ (e.g., Q implies $\Delta J = 0$), where J represents the total angular momentum quantum number (exclusive of nuclear spin). The subscripts indicate the upper state spin-orbit and the lower state spin-spin components, respectively. The progressions are also labeled with N'' , the lower electronic state total angular momentum quantum number (exclusive of nuclear and electron spin). The 2:1 intensity alternation expected for a homonuclear diatomic with nuclear spin of 1 is observed for each of the progressions.

Hamiltonians for $^3\Pi$ and $^3\Sigma$ states have been presented previously; most of the necessary matrix elements may be found in Brown et al.,³⁶ while the spin-spin terms are detailed in Lefebvre-Brion and Field.³⁷ Each rotational level N'' of the lower, $^3\Sigma_u^+$, state is split into three spin-spin components. This state is characterized by the rotational (B , D), spin-rotation (γ), and spin-spin (λ) constants, whereas the additional spin-orbit (A) and Λ -doubling constants (p , q , o) are required to characterize the upper state, $^3\Pi_g$. The spin-orbit interactions split the $^3\Pi_g$ state into three components, and it is determined to be inverted. Each N' level is further split by Λ -doubling. The observed frequencies of 248 spectral lines with $J'' \leq 14$ were least squares fitted³⁸ to calculated line positions by simultaneously diagonalizing the appropriate upper and lower state Hamiltonians in a parity conserving, Hund's case (a) basis to yield the spectroscopic constants listed in Table I. The weighted standard deviation for the fit is 0.029 cm^{-1} , which is expected given the accuracy of our line position measurements. The deduced bond lengths in the $^3\Pi_g$ and $^3\Sigma_u^+$ states are in excellent agreement (ca. 0.5%) with the ab initio predictions;²⁸ the observed term value is in similarly good agreement with the predicted $T_{0,0}$ value. Lines involving levels with $J'' \geq 14$ show progressively larger (observed - calculated) residuals, indicating a perturbation of the lower $^3\Sigma_u^+$ state. The calculated potential energy curves show a number of likely candidates for the perturbing state, and a detailed analysis of this

perturbation is currently in progress.³⁹

The lower state, $^3\Sigma_u^+$, of the observed transition is an electronically excited state which lies $\sim 1.57 \text{ eV}$ above the N_2^{2+} ground $^1\Sigma_g^+$ state as determined by theoretical calculations.²⁸ Several factors contribute to the observation of this excited electronic state in the photofragmentation spectrum. The $^3\Sigma_u^+$ state is efficiently populated via a vertical transition in the electron impact ionization due to the similarities in the bond lengths; the lowest vibrational level of the N_2 ground $^1\Sigma_g^+$ state⁴⁰ and the $^3\Sigma_u^+$ state of N_2^{2+} (present work) have bond lengths of 1.0998 (1) and 1.09406 (8) Å, respectively. Also, the lower state of the transition is expected to be relatively long lived because it is calculated to be bound by 2.3 eV.⁴¹ Lastly, radiative transitions between the $^3\Sigma_u^+$ state and lower energy states are forbidden by electric dipole selection rules. Experimentally, the $^3\Sigma_u^+$ state of N_2^{2+} must live at least 30 μs , since it survives the flight time from the ion source to the interaction region.

On the basis of our data, those of Cosby et al.²⁶ and the calculations of Senekowitsch and O'Neil,²⁸ we conclude that the observed transition occurs between the lowest vibration levels of the two electronic states. The experimental term energy is $15345.933 \text{ cm}^{-1}$, whereas Senekowitsch and O'Neil predict 15342.4 cm^{-1} and a lower state vibrational frequency of 2254 cm^{-1} . If the observed transition were originating from the $^3\Sigma_u^+$, $v = 1$ level, then the calculated term energy must be in error by $\sim 2200 \text{ cm}^{-1}$ and there should be a strong $^3\Pi_g \leftarrow ^3\Sigma_u^+$ (0,0) transition seen at $\sim 17500 \text{ cm}^{-1}$. There is no evidence of such a transition in the spectrum of Cosby et al. These results argue persuasively that the lower electronic state is in $v = 0$. For the upper electronic state, $^3\Pi_g$, only 1 or 2 vibrational levels are expected to be bound.²⁸ On the basis of the spectral profile and structure of the unidentified 16400-cm^{-1} band in the Cosby et al. spectrum,²⁶ it is plausible that this band corresponds to the $^3\Pi_g \leftarrow ^3\Sigma_u^+$ (1,0) transition; the lifetime of the $v = 1$ level is expected to be much shorter than the $v = 0$ level.²⁸ Work is in progress to locate the $v = 1$ levels in both electronic states, and $^{15}\text{N}_2^{2+}$ isotopically substituted spectra will determine the absolute vibrational numbering.³¹

Dissociation from the upper state can occur by either tunneling or electrostatic predissociation. For the former mechanism, the dissociative lifetimes are expected to depend strongly on N . In order to distinguish between these mechanisms, line widths as a function of N for several progressions have been carefully measured, using a single-mode ring dye laser. For the Q_{33} branch, lifetimes range from 60 ps for $N = 5$ to 46 ps for $N = 17$. This weak dependence of the lifetime on N suggests that dissociation occurs through electrostatic interaction with a nearby repulsive electronic state. The ab initio calculations⁴¹ show several possible states that may be responsible for the predissociation. A detailed discussion of the dissociation mechanism will be published.³¹

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(36) Brown, J. M.; Kaise, M.; Kerr, C. M. L.; Milton, D. J. *Mol. Phys.* **1978**, *36*, 553.

(37) Lefebvre-Brion, H.; Field, R. W. *Perturbations in the Spectra of Diatomic Molecules*; Academic Press: Orlando, FL, 1986.

(38) Western, C. M., A General Diatomic Molecule Spectrum Analysis Program, to be published.

(39) Szaflarski, D. M.; Mullin, A. S.; Yokoyama, K.; Western, C. M.; Ashfold, M. N. R.; Lineberger, W. C. *J. Mol. Spectrosc.*, to be published.

(40) Wilkinson, P. G. *Astrophys. J.* **1957**, *126*, 1.

(41) Senekowitsch, J.; O'Neil, S. V. Unpublished results, 1990.