

Observation of the \tilde{A}^1A'' state of isocyanogen

W. Bryan Lynch

Department of Chemistry, University of Evansville, Evansville, Indiana 47722

Hans A. Bechtel, Adam H. Steeves, John J. Curley, and Robert W. Field^{a)}

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 23 April 2007; accepted 7 May 2007; published online 28 June 2007)

The \tilde{A}^1A'' state of isocyanogen, CNCN, is observed using photofragment fluorescence excitation spectroscopy in a room temperature cell and in a molecular beam. The spectra are highly congested, but progressions that correspond to the Franck-Condon active C–N–C bending vibration in the excited state are evident. Linewidth measurements indicate that the excited state lifetime is <10 ps. These measurements are consistent with previous *ab initio* calculations, which predicted a bent excited state with a short lifetime due to predissociation. Although we do not believe that we have observed the origin band of the electronic transition, we place an upper limit of $42\,523\text{ cm}^{-1}$ on the energy of the excited state zero point level. © 2007 American Institute of Physics.

[DOI: 10.1063/1.2745295]

I. INTRODUCTION

Although cyanogen (NCCN) has received considerable attention as a substituent of Titan's atmosphere¹ and was first synthesized in 1815,² the less stable isomer, isocyanogen (CNCN), has been the subject of relatively few studies. Indeed, the first definitive synthesis and spectroscopic identification of CNCN was not reported until 1989.^{3–6} Since then, several experimental and theoretical studies^{7–11} have examined the linear ground electronic state of CNCN. To date, however, there have been no experimental reports of any excited electronic state of CNCN and only two theoretical descriptions^{12,13} of the \tilde{A}^1A'' first excited electronic state. Sherrill and Schaefer's¹² *ab initio* calculations indicate that the \tilde{A}^1A'' state is bent with C–N–C and N–C–N bond angles of 117° and 176° , respectively, and lies at a zero-point to zero-point energy of $T_0=41\,100\text{ cm}^{-1}$, which is somewhat higher than the energy needed ($38\,600\text{ cm}^{-1}$) (Refs. 8 and 14) for dissociation into two $X^2\Sigma^+$ CN fragments. These calculations suggest that the linear to bent electronic transition suffers from extremely poor Franck-Condon factors and that the first excited electronic state of CNCN is predissociative. These predictions, in addition to the difficulty of working with the unstable CNCN molecule, help explain why the first singlet excited electronic state of CNCN has not been observed previously.

Here, we present the first experimental observation of the CNCN \tilde{A}^1A'' state using photofragment fluorescence excitation (PHOFEX) spectroscopy of the $X^2\Sigma^+$ CN photofragments. PHOFEX is a sensitive two-laser technique in which transitions to the excited state of the parent molecule are monitored by excitation and subsequent fluorescence from its photofragments. As shown by Wannemacher *et al.*¹⁴ and Halpern and Huang¹⁵ for NCCN, the PHOFEX technique is ideally suited to photodissociation studies of the $(\text{CN})_2$ iso-

mers because the CN $B^2\Sigma^+$ state fluoresces strongly and is well characterized. Moreover, PHOFEX is expected to be more sensitive than laser induced fluorescence of CNCN because of the predicted predissociation in the excited electronic state. Our measurements are consistent with the theoretical calculations of Sherrill and Schaefer¹² and suggest an excited state lifetime of <10 ps.

II. EXPERIMENTAL SECTION

CNCN was prepared by vacuum pyrolysis of the precursor molecule, *N*-cyano-2,3-diphenylcyclopropeneimine, which was synthesized following the procedure of Yamada *et al.*⁷ and Dubinsky.¹⁶ We made no attempt to purify the precursor by column chromatography or recrystallization, and we found that it could be stored at -50°C for several weeks without any obvious deterioration. The pyrolysis setup consisted of a quartz tube and several traps that were pumped down to 10 mTorr and heated to remove any water. About 300 mg of precursor were pyrolyzed at 450°C under vacuum and the products were collected in a liquid nitrogen cooled trap. Two trap-to-trap distillations (one trap immersed in dry ice/isopropanol, the other in liquid nitrogen) were performed to separate the CNCN product from the less volatile decomposition products of the precursor. After purification, CNCN could be stored in meticulously clean glassware for several days without decomposing. Care was taken to avoid contact with metal surfaces, which have been shown to catalyze the decomposition of CNCN.⁵ The purity of the CNCN sample was determined using infrared spectroscopy (Mattson Infinity Gold Fourier transform infrared spectrometer).

The room temperature sample cell was a glass tube with CaF_2 windows oriented at Brewster's angle on each end. Two methods were used to introduce the CNCN sample into the cell: (1) a Teflon needle valve controlled the flow rate of CNCN to achieve a total pressure of 150 mTorr in the cell

^{a)}Author to whom correspondence should be addressed. Electronic mail: rwfield@mit.edu

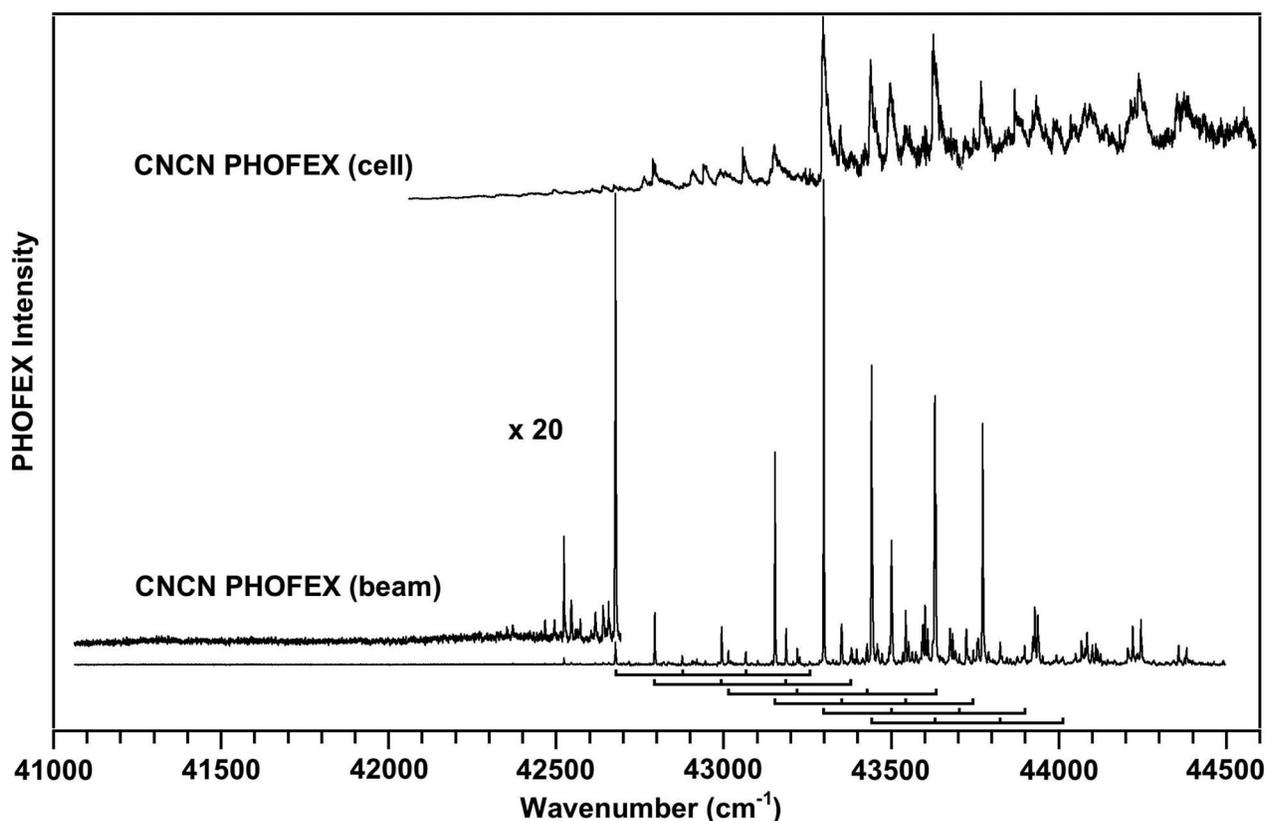


FIG. 1. PHOFEX spectrum of CNCN in a room temperature cell and in a molecular beam.

and (2) the cell was filled with 200 mTorr and replenished every few hours. Both the flow and static methods produced similar PHOFEX spectra.

The molecular beam apparatus consisted of a $12 \times 12 \times 12$ in.³ aluminum vacuum chamber, which was evacuated by a 6 in. diffusion pump (Diffstak 160, Edwards) backed by a rotary mechanical pump. A 10% CNCN:Ar mixture was expanded into the chamber with a 1 mm diameter orifice pulsed valve (Parker Hannifin Corp., General Valve Division, Series 9) with a backing pressure between 400 and 700 Torr. The gas mixture was stored in a glass bulb and connected to the valve with PFA tubing, but no attempts were made to pacify the metal surfaces of the pulsed valve.

The pump and probe lasers were counterpropagated through the cell or molecular beam apparatus and emission was observed at 90° with a photomultiplier tube, which was filtered to minimize scattered laser light. The spectra were obtained by averaging at least 20 laser shots with a LeCroy LC334A oscilloscope interfaced with a LABVIEW program on a personal computer. The pump laser was the doubled (BBO) output of a Lambda-Physik FL3002 dye laser (Coumarin 460, 480) pumped by a Quanta-Ray DCR-3 Nd³⁺:YAG (yttrium aluminum garnet) laser. The probe laser was the doubled (BBO) output of a Lambda-Physik FL2002 dye laser (LDS-765) pumped by a Spectra Physics PRO270 Nd³⁺:YAG laser. For the room temperature cell measurements, the probe laser was fixed to the $P(10)$ CN $B^2\Sigma^+(v'=0) \leftarrow X^2\Sigma^+(v''=0)$ transition and delayed 300 ns after the pump laser, whereas for the molecular beam experiments the probe laser was fixed to the P -branch bandhead and

delayed 50 ns. Delay times were chosen to optimize the observed CN transitions. Typical laser powers were 0.2–1 mJ for the pump laser and less than $1 \mu\text{J}$ for the probe laser. The pump laser was typically operated in a “low resolution” mode with a bandwidth of 0.2 cm^{-1} , but with the insertion of an intracavity étalon, the dye laser could be operated in a “high resolution” mode with a bandwidth of 0.06 cm^{-1} . The spectra obtained at low resolution and high resolution were identical, indicating that the spectral resolution is limited by the lifetime of the electronically excited state and not by the laser frequency bandwidth. Absolute frequency calibration was achieved by simultaneous monitoring of Ne I lines in an optogalvanic cell, whereas relative frequency calibration was achieved by simultaneous monitoring of fringes from a monitor étalon.

III. RESULTS AND DISCUSSION

Figure 1 shows the low resolution PHOFEX spectrum of CNCN between 224 and 244 nm obtained at room temperature and in a molecular beam. No fluorescence from the parent molecule was observed for excitation in this region. The room temperature spectrum is very congested and contains many bands, each of which is quite broad. Individual rotational lines are estimated to have linewidths $>0.5 \text{ cm}^{-1}$ and as a consequence, many of the low- J rotational lines are blended. Additional congestion from hot bands arises because the low frequency C–N–C ground state bend (195 cm^{-1}) is significantly populated at room temperature and is expected to be highly Franck-Condon active.

As shown in Fig. 1, the rotational and hot band congestion is significantly reduced in the jet-cooled spectrum. The spectrum, however, remains exceedingly complicated and congested even at the lowest observed excitation energies, suggesting that the origin band has not yet been observed. Indeed, the first cold band we observe is at $42\,523\text{ cm}^{-1}$, which is $\sim 1420\text{ cm}^{-1}$ higher in energy than the calculated $T_0=41\,100\text{ cm}^{-1}$ of the $\tilde{A}^1A'' \leftarrow \tilde{X}^1\Sigma^+$ origin band.¹² Because the Franck-Condon factors are expected to be poor for the origin band and the molecule is perhaps less predissociated in its lowest vibrational levels, it is possible that we do not yet have the sensitivity to observe the origin band in the PHOFEX spectrum. Instead, we can only place an upper limit on the origin band at $42\,523\text{ cm}^{-1}$. As a consequence, we are unable to provide absolute vibrational assignments. However, we do observe vibrational progressions spaced by about 200 cm^{-1} that are likely progressions of the Franck-Condon active C–N–C excited state bend (ν_5), which has a calculated¹² frequency of 207 cm^{-1} . These progressions are marked with brackets underneath the jet-cooled spectrum in Fig. 1.

In addition to the 200 cm^{-1} progressions, a number of other features in the spectrum compel us to believe that we are observing the excited state of CNCN. First, the infrared spectrum of our postpyrolysis sample is dominated by the very strong CN stretching bands of CNCN (Ref. 5) at 2060 and 2302 cm^{-1} . However, we do see a very weak (by a factor of >170) band at 2157 cm^{-1} which can be attributed to NCCN.⁵ From the infrared intensities, we can estimate a CNCN to NCCN ratio⁹ of about 1.7, indicating that our sample contains a significant amount of NCCN. We also observe an equally weak band at 3311 cm^{-1} which is undoubtedly HCN.¹⁷ Our PHOFEX signal, however, cannot be attributed to NCCN or HCN contaminants because the spectra in Fig. 1 lie well below the NCCN and HCN dissociation limits and even below the energy of the first excited singlet states of NCCN and HCN. We were able to observe the PHOFEX and fluorescence spectrum of the NCCN contaminant, however, at energies above $46\,730\text{ cm}^{-1}$ (214 nm). We obtained spectra in the $\lambda < 214\text{ nm}$ region similar to those previously reported by Halpern and Huang.¹⁵

Second, the carrier of our signal *must* contain at least one CN group for it to contribute to the PHOFEX signal. In addition, we have observed that the PHOFEX signal diminishes with time, indicating that the carrier is unstable, which is in agreement with the known instability of CNCN.¹⁰ We have also observed that the IR bands attributed to CNCN diminish with time, while unassigned weak bands in the C–H region near 3000 cm^{-1} increase with time.

Lifetime measurements of the CNCN excited state are consistent with the *ab initio* calculations of Sherrill and Schaefer,¹² which indicate that the excited electronic state of CNCN lies above the dissociation limit and suggest that the excited state is predissociated. As stated above, the rotational linewidth in our PHOFEX spectra is at least 0.5 cm^{-1} , placing an upper limit on the lifetime of the excited state at only 10 ps . This short lifetime is undoubtedly due to predissociation of the CNCN excited state and explains why no fluorescence is observed from the excited state. In this important

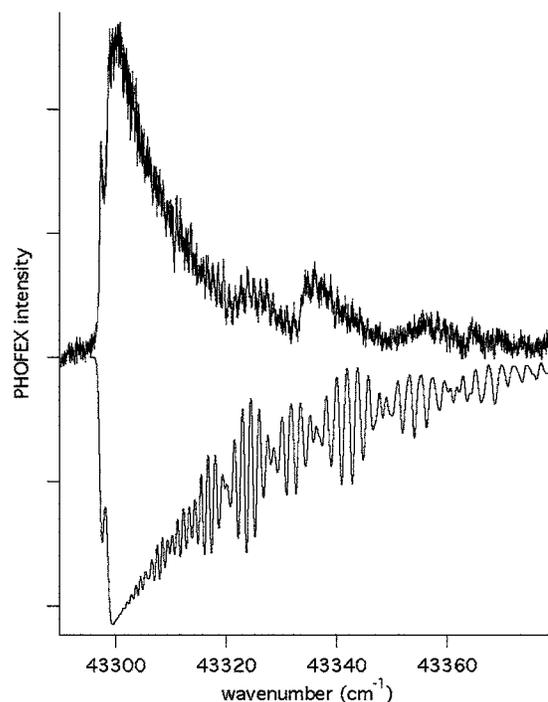


FIG. 2. Room temperature PHOFEX spectrum (top) of the band near $43\,300\text{ cm}^{-1}$ with simulation (bottom). (Absolute frequency calibration was not obtained for this band, so the spectrum was shifted to best correspond to the low resolution scan shown in Fig. 1).

photophysical respect NCCN and CNCN differ; the lower vibrational levels in the excited state of NCCN lie below the dissociation limit and fluorescence is readily observed from them.¹⁵

Finally, the rovibronic band structure is in good agreement with Sherrill and Schaefer's calculations of the bent CNCN excited state geometry.¹² The observed rovibronic bands are blue degraded and are indicative of a linear to bent electronic transition. (Note that the rovibronic band structure of the $\tilde{A}^1\Sigma_u^- \leftarrow \tilde{X}^1\Sigma_g^+$ NCCN transition is red degraded and the excited state is linear.) We have simulated the rotational band structure of the CNCN electronic spectrum with the program SPECVIEW (Ref. 18) using the experimental value for the ground state rotational constant,⁵ $B''=0.172\,59\text{ cm}^{-1}$, the rotational constants determined from the geometry calculated by Sherrill and Schaefer at the TZ2P CISD level of theory:¹² $A'=2.455\text{ cm}^{-1}$, $B'=0.2054\text{ cm}^{-1}$, $C'=0.1895\text{ cm}^{-1}$, and a linewidth of 0.5 cm^{-1} . Figure 2 shows the SPECVIEW simulation and the observed PHOFEX band near $43\,300\text{ cm}^{-1}$ obtained at room temperature. Like the observed bands, the band in the simulation is blue degraded, and the agreement in band contours is quite good. However, due to the presence of multiple overlapping bands, we have not attempted to fit the band contour to obtain improved rotational constants.

IV. CONCLUSIONS

We have synthesized CNCN by vacuum pyrolysis of *N*-cyano-2,3-diphenylcyclopropenimine and observed an electronic spectrum of CNCN for the first time. Many features of the spectrum are consistent with previous *ab initio*

calculations of a bent electronic excited state. The spectrum, however, is highly congested and not completely assignable at this time. Additional measurements, such as double resonance techniques, may aid in assignments by labeling the lower state, thereby providing complete discrimination against hot band transitions.

ACKNOWLEDGMENTS

Two of the authors (W.B.L. and H.A.B) acknowledge the Donors of the American Chemical Society Petroleum Research Fund for support, and another author (A.H.S.) acknowledges the Army Research Office. This work was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy (DE-FG0287ER13671).

¹V. G. Kunde, A. C. Aikin, R. A. Hanel, D. E. Jennings, W. C. Maguire, and R. E. Samuelson, *Nature (London)* **292**, 686 (1981).

²L. J. Gay-Lussac, *Ann. Chim. (Paris)* **95**, 175 (1815).

³T. van der Does and F. Bickelhaupt, *Angew. Chem., Int. Ed. Engl.* **27**, 936 (1988).

⁴O. Grabandt, C. A. de Lange, R. Mooyman, T. van der Does, and F. Bickelhaupt, *Chem. Phys. Lett.* **155**, 221 (1989).

⁵F. Stroh and M. Winnewisser, *Chem. Phys. Lett.* **155**, 21 (1989).

⁶L. S. Cederbaum, F. Tarantelli, H.-G. Weikert, M. Scheller, and H. Koppel, *Angew. Chem., Int. Ed. Engl.* **28**, 761 (1989).

⁷K. M. T. Yamada, M. W. Markus, G. Winnewisser, W. Joentgen, R. Kock, E. Vogel, and H.-J. Altenbach, *Chem. Phys. Lett.* **160**, 113 (1989).

⁸P. Botschwina and P. Sebald, *Chem. Phys.* **141**, 311 (1990).

⁹F. Stroh, B. P. Winnewisser, M. Winnewisser, H. P. Reisenauer, G. Maier, S. J. Goede, and F. Bickelhaupt, *Chem. Phys. Lett.* **160**, 105 (1989).

¹⁰M. Winnewisser, J. W. G. Seibert, and K. M. T. Yamada, *J. Mol. Spectrosc.* **153**, 635 (1992).

¹¹See, for example, M. T. Nguyen, *Chem. Phys. Lett.* **157**, 430 (1989); K. K. Sunil, J. H. Yates, and K. D. Jordan, *ibid.* **171**, 185 (1990); P. Botschwina and J. Flugge, *ibid.* **180**, 589 (1991); M. C. L. Gerry, F. Stroh, and M. Winnewisser, *J. Mol. Spectrosc.* **140**, 147 (1990); F. Stroh, M. Winnewisser, and B. P. Winnewisser, *Can. J. Phys.* **72**, 1251 (1994); *J. Mol. Spectrosc.* **162**, 435 (1993); Y. H. Ding, X. R. Huang, Z. S. Li, and C. C. Sun, *J. Chem. Phys.* **108**, 2024 (1998).

¹²C. D. Sherrill and H. F. Schaefer III, *J. Chem. Phys.* **100**, 8920 (1994).

¹³R. K. Chaudhuri, S. L. N. G. Krishnamachari, and K. F. Freed, *J. Mol. Struct.: THEOCHEM* **768**, 119 (2006).

¹⁴E. A. J. Wannemacher, H. Lin, and W. M. Jackson, *J. Phys. Chem.* **94**, 6608 (1990).

¹⁵J. B. Halpern and Y. Huang, *Chem. Phys.* **222**, 71 (1997).

¹⁶I. A. Dubinsky, Ph.D. thesis, Massachusetts Institute of Technology, 1998.

¹⁷G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand, New York, 1966), Vol. III.

¹⁸SPECVIEW, simulation and fitting of rotational structure of electronic and vibronic bands; V. L. Stakhursky and T. A. Miller, 56th Molecular Spectroscopy Symposium (<http://www.chemistry.ohio-state.edu/~vstakhur>).