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Simultaneous one and twophoton processes in the photodissociation of NCNO using a tunable dye laser

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case (a) limit, at least in a two-body model. The spin-orbit state selectivity might then be related to how the case (e) states[13] at large Ca–Cl$_2$ separations evolve into case (a) states. This model suggests that production of CaCl($X\,^2\Sigma^+$) and CaCl* will exhibit the same spin-orbit state dependence as the chemiluminescent channel.

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Simultaneous one- and two-photon processes in the photodissociation of NCNO using a tunable dye laser[a]

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State-to-state studies of the photodissociation of polyatomic molecules can provide valuable information regarding fragment yields and quantum state distributions. Such information is often prerequisite to understanding the dynamics of dissociation and the nature of the excited potential sufrace(s). In this communication, we report data indicating that NCNO will be a very important test molecule for theoretical models of photodissociation dynamics. It has the desirable characteristics of nitroso compounds,[1] a low C–NO dissociation energy (29 kcal mol^{-1}),[2] an $\pi^* - n$ ($S_1 - S_0$) transition in the region 500–880 nm (which in some nitroso compounds has been shown to be predissociative),[3-6] and an NO fragment which can be monitored by laser induced fluorescence (LIF).[3,4] In addition, the CN fragment can be easily detected by LIF,[7] and thus E, V, R, T energy distributions in both fragments can be determined.[8]

Our initial results on the photodissociation of NCNO in the region 660–732 nm show that direct excitation to a state different than S_1 is responsible for the dissociation of NCNO following one-photon absorption at wavelengths < 720 nm. In addition, throughout the region 660–732 nm, a second photon can easily excite the initially prepared S_1 state, thereby leading to rapid and efficient dissociation. However, it is straightforward to distinguish between one-photon dissociation, which produces rotationally "cold" CN radicals, and the resonant two-photon dissociation, which produces rotationally "hot" CN radicals.

NCNO tends to detonate violently when impure[9] and was prepared as reported elsewhere.[10] The experimental arrangement has been described previously.[3] Briefly, it consists of two counterpropagating unfocused laser beams: a Nd:YAG laser pumped dye laser operating with LDS698 dye (660–732 nm, < 12 mJ pulse^{-1}) as the photolysis laser, and a N$_2$ laser pumped dye laser operating with BBQ dye (373–399 nm, < 10 μJ pulse^{-1}) as the probe laser for CN LIF. The beams are viewed at right angles with two PMT's facing one another; a PMT coupled with a Schott RG830 filter allows detection of NCNO fluorescence in the 750–890 nm region, and a PMT equipped with an interference filter (388.3 ± 5 nm) is used to detect CN($B - X$, $\Delta v = 0$) fluorescence. Signals from the two PMT's are simultaneously observed with a dual channel digital oscilloscope interfaced to a computer which controls the experiment and processes the data. The delay between the two lasers is determined by a delay generator with 10 ns resolution, and the jitter is ±10 ns. Gaseous NCNO (typically 5 mTorr) is flowed continuously in order to replenish the sample for each laser firing.

Figure 1(A) presents the LIF spectrum of NCNO, and all of the peaks correspond to known NCNO absorption features.[11] The CN LIF signal monitored at $J=2$ [Fig. 1(C)] shows clearly that the production of CN($J=2$) does not follow the S_1-S_0 absorption features. Both signals vary linearly with the photolysis laser intensity, confirming that one-photon excitation occurs in each instance. However, the NCNO fluorescence lifetime (660–732 nm) is ≥ 11 μs, whereas the CN($J=2$) appearance time is <20 ns. These observations indicate the existence of an additional state which is responsible for direct dissociation.[12] Absorption to this state is apparently weak and hidden in the congested spectrum attributed to the $\pi^* \leftarrow n$ transition.[8,11]

The LIF spectrum of nascent CN [Fig. 2(A)] is that of an extremely cold, non-Boltzmann, rotational distribution with 60% of all CN radicals in $J=0-4$, and photodissociation at 532 nm shows that rotational distributions for CN and NO[8] are similar to one another. This indicates very efficient conversion of the rotational angular momentum of the room temperature NCNO into orbital angular momentum of the photofragments during the dissociation process. This is characteristic of dissociation which follows direct excitation to a repulsive state.

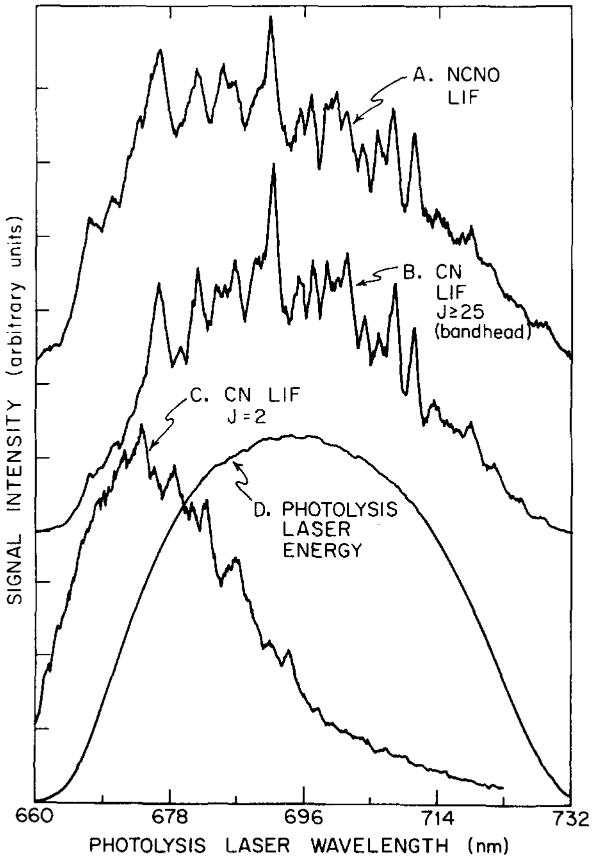

FIG. 1. NCNO fluorescence and CN yields, obtained via LIF, as a function of the photolysis laser wavelength. (A) and (B) show the NCNO fluorescence and the hot CN yield (measured at the bandhead $J\geq 25$), respectively; both spectra are observed simultaneously and exhibit peaks corresponding to the NCNO absorption features ($E_{\text{laser}}<12$ mJ/pulse). (C) shows the cold CN yield spectrum (measured at $J=2$) attributed to one-photon direct dissociation ($E_{\text{laser}}<0.3$ mJ pulse^{-1}). The spectra are not corrected for the variation in laser energy, which is shown in (D). The delay between the lasers was 50 ns, and the pressure was 5 mTorr.

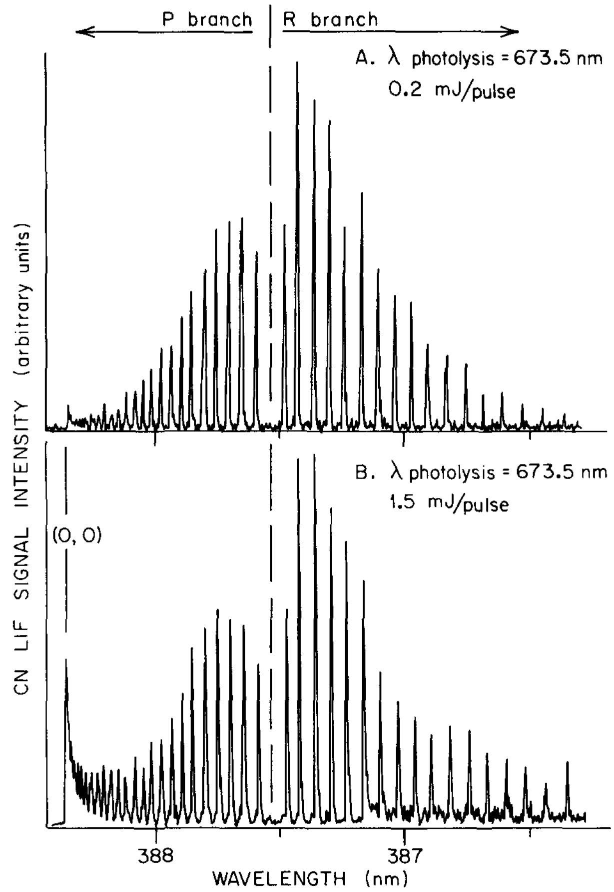

FIG. 2. CN LIF spectra observed following 673.5 nm photolysis. In (A) the photolysis laser energy is 0.2 mJ and the cold spectrum peaks at $J=2$ (the peak for room temperature CN is at $J=7$); in (B), the photolysis laser energy is 1.5 mJ; notice the appearance of the bandhead at $J\geq 25$ (see the text).

Increasing the photolysis laser intensity results in the appearance of highly rotationally excited CN, in addition to the cold CN radicals [Fig. 2(B)]. The facts that (a) the hot CN LIF signal intensity (monitored at the bandhead) depends quadratically on the photolysis laser intensity, and (b) a scan of the CN yield (monitored via LIF at the bandhead) as a function of photolysis laser wavelength exhibits peaks similar to those in the NCNO LIF spectrum [Fig. 1(B)], constitute proof that the hot CN is produced via resonant two-photon excitation ($S_0 \rightarrow S_1 \rightarrow$ dissociative state). Additional evidence for this two photon dissociation process comes from our ability to produce the hot part of the CN spectrum, but not the cold part, by one-photon excitation at 355 nm.

Further experiments are in progress in order to identify the state(s) which lead to dissociation and to clarify the dynamics.

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NOTES

An *ab initio* SCF calculation of the polarizability tensor of sulphur dioxide

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The principal components of the dynamical polarizability tensor of SO_2 at the optical wavelength $\lambda = 5145$ Å have been recently determined experimentally by Murphy.[1] The procedure consisted of combining literature values of the average polarizability $(\bar{\alpha})$ and the Raleigh depolarization ratio[2] with possible values of the polarizability tensor component ratio so as to reproduce the Raman contours of the pure rotational spectrum of SO_2. Two sets of numerical values for the principal components are compatible with the results of the above experiments, corresponding to positive and negative values of the quantity $\alpha_{xx} - \bar{\alpha}$, where α_{xx} is the principal polarizability component along the dipole axis. As discussed by Murphy,[1] the negative sign for $\alpha_{xx} - \bar{\alpha}$ is the preferred one, partly on the basis of a negative Kerr constant,[3] provided the Kerr constant is not dominated by the first hyperpolarizability, and partly by intuition since the molecule is expected to be most polarizable along its bonds and least so perpendicular to the molecular plane.

In this note the results of an *ab initio* Hartree–Fock SCF calculation of the static polarizability $(\lambda = \infty)$ are presented which are believed to be sufficiently accurate to determine the sign of $\alpha_{xx} - \bar{\alpha}$ and decide in favor of one of Murphy's assignment for the polarizability tensor. In agreement with Murphy's choice, the sign of $\alpha_{xx} - \bar{\alpha}$ is found to be negative.

The components of the polarizability tensor were evaluated by the coupled perturbed Hartree–Fock (CPHF) method,[4–6] which is equivalent to the finite field Hartree–Fock method in the limit of vanishing applied electric field strength.[7] Briefly stated, the CPHF method allows the calculation of the first order change to the SCF occupied orbitals and the corresponding second order energy change within the Hartree–Fock formalism. In this work, as is the usual practice, the first order change to the doubly occupied orbitals is expanded in terms of the unperturbed virtual orbitals. The unperturbed SCF calculations were performed using the MOLECULE supermatrix package of Almlöf[8] and a new, symmetry blocked version of the quadratically convergent SCF (QC-SCF) program.[9] The same QC-SCF program was then used for the CPHF calculations, as already discussed in detail elsewhere.[9] The number of CPHF iterations needed per polarizability component was six to achieve six significant figure accuracy. The basis set for the S atom is the (11*s*, 7*p*) Gaussian basis of Huzinaga,[10] contracted to [6*s*, 5*p*] as recommended by Dunning and Hay,[11] except contracting the *p*'s as (3, 1, 1, 1, 1), and extended by a diffuse *sp* set $(\zeta = 0.05)$ and three sets of Cartesian 3*d* functions $(\zeta_1 = 0.60,\ \zeta_2 = 0.20,\ \zeta_3 = 0.07)$. The oxygen basis is Dunning's[12] (9*s*, 5*p*) set contracted to [4*s*, 3*p*] and extended by a diffuse *sp* set $(\zeta = 0.08)$ and two sets of Cartesian 3*d* functions $(\zeta_1 = 0.8,\ \zeta_2 = 0.2)$. Note that the 3*d* sets comprise of six functions i.e., the basis contains the 3*s* type $x^2 + y^2 + z^2$ orbitals, while the diffuse *sp* sets contain a 1*s* and the set of three 2*p* orbitals with the same exponent. The full contracted basis is thus [7*s*, 6*p*, 3*d*; 5*s*, 4*p*, 2*d*], corresponding to a total of 101 basis orbitals. The diffuse *s*, *p*, and *d* functions were chosen in order to describe the polarizability adequately, as discussed in detail elsewhere,[14–20] while the 3*d* orbitals with the highest exponents are roughly optimal on energetic grounds.[17,21]

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