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The photodissociation of carbonyl cyanide $CO(CN)_2$ at 193 nm studied by photofragment translational energy spectroscopy

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The photodissociation of carbonyl cyanide $CO(CN)_2$ at 193 nm was investigated by photofragment translational energy spectroscopy. For all the fragments created (CO, CN, OCCN, NCCN), the kinetic energy distributions were measured and two decay channels identified. The radical decay, $CO(CN)_2 + h\nu \rightarrow OCCN + CN$, dominates with a yield of 94% ± 2% and shows the available energy mainly (82%) channeled into the internal degrees of freedom of the fragments. A fraction of 18% ± 6% of the nascent OCCN radicals has sufficient energy to spontaneously decay to CO+CN involving a barrier ≤160 kJ/mol. With a yield of 6% ± 2% the molecular decay produces the fragments CO+NCCN. These fragments acquire a high available energy owing to the formation of the new C–C bond in NCCN. An average fraction of 70% is partitioned into internal fragment energy. Even the fastest fragments are still internally hot, indicating that with the high barrier expected, a substantial exit channel interaction is operative. The isotropic recoil distribution found for the products CN, OCCN, and NCCN further suggests that both the radical and the molecular decay are, on the time scale of a parent rotation, slow and probably indirect. © *1999 American Institute of Physics*. [S0021-9606(99)00927-7]

I. INTRODUCTION

Carbonyl cyanide $CO(CN)_2$ (Fig. 1, insert) has recently attracted attention as precursor for the OCCN radical.¹ As various carbonyl and cyano-containing polycarbon molecules have been identified in the interstellar medium^{2,3} the existence of this radical is of interest in astrophysics and it may also play a role in combustion processes. In a preliminary study¹ we focused on the preparation and stability of the photofragment OCCN. Following photolysis of $CO(CN)_2$ in the gas phase at 193 nm, it was shown that dissociation proceeds primarily as

$$CO(CN)_2 + h\nu \rightarrow OCCN + CN.$$
 (1a)

Only about 25% of the nascent OCCN fragments have sufficient internal energy for a spontaneous decay according to

$$OCCN \rightarrow CO + CN.$$
 (1b)

The simple generation of a large fraction of stable OCCN radicals was thus demonstrated, allowing this species to be studied by spectroscopic methods or used as a reactant for synthetic purposes. Prior to this study, OCCN has not been prepared by photolysis and the only previous observation was in a neutralization-reionization experiment by reduction of the OCCN⁺ cation.⁴ Francisco and Liu⁵ have recently reported results of *ab initio* calculations on stability, structure and vibrational frequencies, and an experimental investigation on the spectroscopy of this interesting radical is in progress.⁶

The aim of the present work was to establish the decay mechanism of isolated $CO(CN)_2$ following excitation at 193

nm. The molecule consists of three strongly bound groups, a CO and two CN moieties, connected by two comparatively weak C–C single bonds. Beside the simple radical decay with an α -cleavage (1a), a molecular decay

$$CO(CN)_2 \rightarrow CO + NCCN,$$
 (2)

favored by a symmetric substitution of the parent molecule, may be operative involving scission of the two α -C-C bonds and the simultaneous formation of the new C-C bond of the NCCN product. Molecular decays have been observed for a number of molecules⁷⁻¹⁰ and probably most extensively studied in the case of formaldehyde H₂CO.⁷ To our knowledge, the systems reported so far were limited to the association of two atoms to a diatomic, whereas CO(CN)₂ would decay to a four atomic molecule requiring a complex transition state with substantial changes of bond angles and distances. The equivalence of the α -C-C bonds also makes carbonyl cyanide a candidate for a three-body decay,^{11,12}

$$CO(CN)_2 \rightarrow CO + CN + CN,$$
 (3)

where the two bond cleavages occur in a single kinetic step. For such a dissociation process one distinguishes between a synchronous concerted and an asynchronous concerted reaction depending whether the dissociation dynamics follows a synchronous or an asynchronous bond breaking of the two identical bonds.^{11,12}

To investigate the full picture of the photochemical decay paths of $CO(CN)_2$ we used photofragment translational energy spectroscopy (PTS).^{13,14} We were able to detect all the generated fragments (CO, CN, OCCN, and NCCN) and to measure their kinetic energy distributions as well as the pertinent fragment recoil anisotropies.

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FIG. 1. Gas phase absorption spectrum of carbonyl cyanide $CO(CN)_2$ in the wavelength range 190–410 nm. The spectrum was recorded at room temperature using a vapor pressure of 2 mbar and a resolution of about 0.2 nm (FWHM).

II. EXPERIMENT

The experiments were carried out with a photofragment translational energy spectrometer described in detail elsewhere.¹⁵ A pulsed laser beam is directed along the rotation axis of a pulsed molecular beam source which rotates in a plane with the fixed detection axis. The variable angle between the molecular beam and the detection axis is denoted as the scattering angle Θ . Following a flight path of 34.5 cm, the neutral fragments created in the intersection region of the laser and the molecular beam are ionized by electron bombardment and mass-filtered by a quadrupole mass spectrometer (Balzers QMA 160). The ion signal from a secondary electron multiplier was fed into a multichannel scaler (Stanford Research SR 430, 1.28 μ s bin width, 1024 channels). The experiments were performed at 193 nm with an ArF excimer laser (Lambda Physik Compex 102, repetition rate 20 Hz). The photolysis laser crossed the molecular beam at a distance of 65 mm from the pulsed nozzle and 45 mm from the skimmer. The laser beam was slightly focused to an elliptical spot, ≈ 2 mm along the detection axis and ≈ 6 mm perpendicular to the detection axis, at the intersection with the molecular beam. The time-of-flight (TOF) spectra were recorded with laser fluences ranging from 10 to 100 mJ/cm². The probability for multiphoton absorption at fluences ≤ 20 mJ/cm² was found to be very low, as expected from the absorption cross section at 193 nm and the corresponding saturation factor. A distinctive effect of multiphoton processes was observed only at $\geq 50 \text{ mJ/cm}^2$.

The TOF distributions were recorded with unpolarized laser light at scattering angles $\Theta = 9$, 30 and 60°. Particularly severe at $\Theta = 9^{\circ}$, the interfering background signal from parent molecules cracked in the ionizer, was subtracted on a shot-to-shot basis by leaving every second molecular pulse unphotolyzed. The TOF distributions presented in this article were corrected for the ion flight times through the mass filter.

The recoil anisotropy β of the fragments^{13,15} CN, OCCN, and (CN)₂ was measured at six different polarization

angles (as defined between the electric field vector of the laser and the detection axis). For this purpose, the excimer laser beam was directed through a stack of ten quartz plates at Brewster's angle generating linearly polarized light with a polarization degree of $92\% \pm 1\%$.

Carbonyl cyanide CO(CN)₂ was synthesized and purified according to a published procedure¹⁶ by reaction of tetracyanoethylene oxide with n-butyl sulfide at 50 °C. The yellowish liquid with a boiling point of 66 °C was purified by multiple distillation at reduced pressure. Premixed gas samples of 2% CO(CN)₂ in 350 mbar He were expanded through a piezoelectrically actuated valve (orifice 0.5 mm and opening angle 140°) providing molecular pulses of 100 μ s. The concentration of clusters $[CO(CN)_2]_n$ in the molecular beam pulses was found to be negligible under these expansion conditions. The onset of clustering occurs at He stagnation pressure ≥ 800 mbar.¹⁷ The delay between the opening of the nozzle and the photolysis pulse was kept fixed to probe the molecular beam pulse $\approx 30 \ \mu s$ after its onset. The stream velocity of the pulses was determined before and after each photodissociation measurement using a chopper wheel synchronized with the pulsed valve. The width of the velocity distribution corresponds to a translational temperature of ≈ 4 K.

III. RESULTS

A. UV spectrum

The absorption spectrum of CO(CN)₂ in the range 190-400 nm, shown in Fig. 1, exhibits a weak band system with a maximum at around 330 nm and a strong absorption below 230 nm. The weak band system, which is due to the S_0 $\rightarrow S_1(n\pi^*)$ transition localized on the CO group, is highly structured. At least ten evenly spaced vibronic bands can be distinguished in the range 270-400 nm. The spacing is initially about 1230 cm⁻¹ and decreases with increasing excitation. Prochorow et al.¹⁸ have analyzed the spectrum in some detail and assigned this progression to the C=O stretching vibration in the S_1 state guided by the results of acetone. Each of these bands is further split into eight distinct, narrow peaks spaced by $\approx 128 \text{ cm}^{-1}$. They are most likely due to the excited state in-plane δ (N-C-C-C-N) bending mode (a_1) , whose corresponding ground state frequency is 127 cm^{-1} .

Besides the $n\pi^*$ transition, a strong, presently unassigned absorption starts at around 230 and extends to 190 nm, the lower limit of our ultraviolet (UV) measurement. This absorption very probably involves a Rydberg transition to the ${}^1(n,3s)$ state by analogy with other carbonyl compounds.^{19–21} Our photolysis experiments were carried out at 193 nm, where the absorption cross section $\epsilon \approx 2300 \,\mathrm{dm^3 \,mol^{-1} \, cm^{-1}}$ ($\sigma = 8.7 \times 10^{-18} \,\mathrm{cm^2}$), about 1000 times greater than at the maximum of the $n\pi^*$ transition.

B. TOF spectra of (CN)₂ and OCCN

Photofragments were collected at $m/e = 26(\text{CN}^+)$, $28(\text{CO}^+)$, $52[(\text{CN})_2^+]$, and $54(\text{OCCN}^+)$. At the mass filter setting m/e = 54 and 52, the species OCCN and $(\text{CN})_2$ from the primary dissociation steps (1a) and (2), respectively, con-



FIG. 2. TOF distributions of NCCN fragments (m/e = 52) measured at scattering angles 9 and 60° after unpolarized excitation of CO(CN)₂ at 193 nm. The solid lines through the data points were calculated from the translational energy distribution $P(E_T)$ shown in Fig. 3(a) as a dashed line which coincides with the solid line above 80 kJ/mol.

tribute exclusively to the signal. The signals at m/e = 26 and 28, however, may originate from primary dissociation (1a) and (2), secondary dissociation of OCCN (1b), or cracking of OCCN and (CN)₂ in the ionizer of the detection system. In the fit procedure, the unambiguous TOF spectra of OCCN⁺ and $(CN)_2^+$ were therefore analyzed first. The center-of-mass kinetic energy distributions $P(E_T)$ obtained from these fits²² were then used to calculate the TOF profiles of the counter-fragments CN and CO, respectively, based on the strict momentum-correlation of the fragment pairs.

In the TOF spectra monitored at m/e = 52 and shown in Fig. 2, the signal stems exclusively from the fragment $(CN)_2$. The spectra were recorded at scattering angles Θ = 9 and 60°. The solid lines represent the best fit obtained by forward convolution²² of the center-of-mass kinetic energy distribution $P(E_T)$. The latter is displayed in Fig. 3(a) as a dashed curve. As will be discussed below, this $P(E_T)$ represents not the full distribution which is given by the solid line, but only a truncated part of it. The missing part below E_T ~80 kJ/mol is due to the slow (CN)₂ fragments which possess sufficient internal energy to decay spontaneously into CN+CN before reaching the detector.

The same fitting procedure was applied to the TOF spectrum recorded at m/e=54 shown in Fig. 4 where only OCCN fragments contribute to the signal. The solid line was obtained from the dashed $P(E_T)$ curve in Fig. 3(b). Similar to the result for $(CN)_2$ above, this $P(E_T)$ represents the stable OCCN fragments which reach the detector without undergoing secondary dissociation. A rough first estimate of the branching ratio between the primary channels leading to OCCN+CN (1a) and to $(CN)_2$ +CO (2) is obtained by comparison of the relative signal strengths at m/e=54 and 52. Assuming the ratio of the ionization efficiencies of OCCN to



FIG. 3. Center-of-mass translational energy distributions $P(E_T)$ for the photoinduced decay of $CO(CN)_2$ to (a) CO+NCCN (molecular channel), and (b) CN+OCCN (radical channel). The dashed lines which coincide at higher E_T with the solid lines represent truncated $P(E_T)$'s used to fit by forward convolution the TOF profiles of NCCN⁺ and OCCN⁺, respectively. The arrows mark the available energy of the fragment pairs.

 $(CN)_2$ to be 0.97, as calculated from the sum of atomic polarizabilities,²³ and correcting for the dependence of the detection efficiency on kinematic factors,²² we obtain a ratio OCCN/ $(CN)_2 \approx 15$. This estimate has, however, a substantial uncertainty due to the neglect of the secondary dissociation



FIG. 4. TOF distributions of OCCN fragments (m/e=54) measured at $\theta = 9$ and 30° after unpolarized excitation of CO(CN)₂ at 193 nm. The solid lines are forward convolution fits using the truncated $P(E_T)$ shown in Fig. 3(b).



FIG. 5. Unpolarized TOF spectra of $m/e = 26(CN^+)$ at $\Theta = 9$ and 60° . The contributions from primary dissociation to CN+OCCN (thin solid line), secondary dissociation of OCCN (dotted line), and OCCN cracking in the ionizer (dash-dotted line) are shown. The primary CN coincident with stable OCCN is indicated with a thin dashed line in the $\Theta = 9^\circ$ spectrum.

and the differences in the amount of cracking of OCCN and $(CN)_2$. A refined calculation of this branching ratio is presented later in the text.

C. TOF spectra of CN

The TOF profiles of the CN⁺ fragments are displayed in Fig. 5. These spectra contain three different contributions, namely the CN from the primary process (1a), the CN from the secondary decay of OCCN (1b) and the CN from cracking of OCCN in the detector. In this order the kinetic energy of CN is expected to decrease. The dashed line in the Θ = 9° spectrum was calculated with the $P(E_T)$ obtained from channel (1a) for the counterfragment OCCN [dashed line in Fig. 3(a)]. It is evident that this $P(E_T)$ curve only reproduces the fast part of the CN⁺ spectrum while a slow contribution is missing. With the total $P(E_T)$ that also considers the internally hot OCCN fragments which decay before reaching the detector [given as a solid curve in Fig. 3(a)], we obtain the total signal contribution from the primary CN fragment. This is displayed by the thin solid lines in Fig. 5.

The dotted line represents the CN contribution from the secondary decay of OCCN to CO+CN (1b). The $P(E_T)$ of these unstable OCCN radicals prior to their secondary decay was obtained by subtracting the truncated $P(E_T)$ fitted to the OCCN TOF spectra from the total primary $P(E_T)$ in Fig. 3(b). The process following the secondary bond cleavage was calculated using the procedure given in Refs. 24–26 and a kinetic energy distribution of the CO+CN pairs which is symmetrically centered at 30 kJ/mol [full width at half maximum (FWHM) = 20 kJ/mol]. This value is a rough estimate based on the dissociation energies of $410^{27,28}$ and 126 kJ/mol^{5,27} for (1a) and (1b), respectively, leaving a maximum available energy for secondary CO+CN of 93 kJ/mol.

Furthermore, we assumed a forward-backward symmetric angular distribution of these fragments and a statistical decay^{24,25} implying a lifetime of the unstable OCCN longer than one rotational period. The unstructured TOF spectra of CN^+ do not justify a refined fit of the secondary decay process.

The third contribution to the m/e = 26 signal, which stems from dissociative ionization of OCCN in the detector and indicated by a dash-dotted line in Fig. 5, can be determined straightforwardly since the cracking pattern of OCCN is known. Under our experimental conditions the relative signals were measured to be $OCCN^+/CN^+/CO^+ \sim 55/30/15$. (We determined this ratio in a separate experiment using methyl cyanoformate, NCCOOCH₃, which yields 98% of OCCN+OCH₃ after photolysis at 193 nm. Consequently, the CN⁺ and CO⁺ signals measured in this case originate almost exclusively from cracking. The OCCN fragments from $CO(CN)_2$ and NCCOOCH₃ are expected to have essentially the same cracking patterns since their average internal energies, about 170 and 150 kJ/mol, are not much different.) Furthermore, the OCCN⁺ \rightarrow CN⁺ cracking contribution was considered to have the same shape as the OCCN⁺ profile in Fig. 4 except for a small delay owing to the different ion flight times.¹⁵ This is supported by the findings that the dependence of the cracking on the internal energy of OCCN is negligible; TOF spectra measured at ionization energies of 70, 90, and 120 eV, spanning a much larger range than the internal energies of the OCCN fragments (≈ 0.5 eV), were identical. It is noted that the OCCN cracking contribution to the CN⁺ signal in Fig. 5 appears only at $\Theta = 9^{\circ}$ but vanishes at $\Theta = 60^{\circ}$ because the OCCN fragments are too slow to reach the detector at this angle.

A last, but negligible source of CN^+ , is dissociative ionization of $(CN)_2$. In a separate experiment we used a pure cyanogen (NCCN) expansion and determined the ratio of the ion signals $CN^+/(CN)_2^+$ to be ≈ 0.2 . The photoproduct $(CN)_2$ has a yield of about 6%, as estimated in the previous section. The relative contribution to m/e = 26 from $(CN)_2$ cracking is therefore two orders of magnitude smaller than the contribution from primary CN fragments.

Thus the best fit to the TOF spectrum of CN^+ given by the strong solid line in Fig. 5 was calculated iteratively by changing the total primary $P(E_T)$ in small steps, evaluating the resulting contributions from (1a) and (1b) by forwardconvolution, and adding the cracking contribution. The finally obtained total TOF profile represents then the sum of all the contributions indicated by the thin solid line, the dotted line and the dash-dotted line shown in the upper part of Fig. 5.

Given the negligible contribution of $(CN)_2$ cracking to the m/e = 26 signal, our preliminary analysis of the CN^+ spectra is found to be basically correct.¹ The fit is now slightly modified with regard to the relative weight of the CN^+ contribution from secondary dissociation of OCCN (1b) and dissociative ionization of OCCN. Having determined the latter we can now quantify the OCCN cracking contribution to the CN^+ signal and in turn the fraction of unstable OCCN radicals which undergoes secondary fragmentation following (1a). Accordingly, this fraction is esti-



FIG. 6. Unpolarized TOF spectra of $m/e = 28(\text{CO}^+)$ at $\Theta = 30$ and 60° . The CO⁺ contributions from the molecular channel (thin solid line), secondary dissociation of OCCN (dotted line) and from OCCN cracked in the ionizer (dashed line) are shown. The sum of the three components is indicated by a bold solid line reproducing the measured spectrum.

mated from the ratio of the integrated areas of the truncated curve to the total $P(E_T)$ in Fig. 3(b) and found to be 18% $\pm 6\%$. The relatively large error of $\pm 6\%$ is due to the uncertainty in the overlapping contributions of the CN⁺ from the secondary decay and the cracking of OCCN.

D. TOF spectra of CO

The m/e = 28 spectra obtained at $\Theta = 30$ and 60° are displayed in Fig. 6. By recording these spectra (and also those at m/e=26), it was important to lower the laser fluence to $\leq 20 \text{ mJ/cm}^2$ to avoid two-photon absorption contributions to the signal. At higher fluences the intensity of a fast signal component appeared between 50 and 150 μ s flight time, growing much faster with fluence than the rest of the signal. This was attributed to laser-induced secondary decay of OCCN, since it only appeared at the ion masses of CN and CO, but not at those of OCCN or (CN)₂.¹ With 10 mJ/cm², the spectra in Fig. 6 were found to have three components. The fastest CO^+ part, centered at around 100 μ s, stems from the molecular channel (2). The $P(E_T)$ obtained from the fit of the corresponding counterfragment (CN)2 was used to calculate this contribution (thin solid lines in Fig. 6). The fit is in good agreement with the rising edge and the fast peak of the m/e=28 spectra. The second contribution (dotted line) is from the spontaneous secondary decay of OCCN (1b) and the third contribution (dashed line) is from dissociative ionization of OCCN. Similarly to the analysis of the CN⁺ spectrum above, the contributions from spontaneous dissociation and cracking of OCCN strongly overlap in the CO⁺ spectrum recorded at small scattering angle. The ratio of CO^+ from (1b) to OCCN cracking (~18 to ~16%) is close to unity. It is noted that the detection of the CO^+ cracking fragments is kinematically unfavorable so that the OCCN cracking contribution is weak at $\Theta = 30$ and vanishes at $\Theta = 60^{\circ}$.

The bold solid line in Fig. 6 represents the sum of the contributions from the molecular channel (2), the spontaneous decay (1b) and from the cracking of primary OCCN products. The contributions from spontaneous decay and cracking of OCCN were calculated without further adjustments, as described in Sec. IIIC and added with relative weights of 2:1, respectively, which are given by the OCCN cracking ratio and the branching of channel (1a) and (2). The thin solid line in Fig. 6 represents the forward convolution of the $P(E_T)$ shown by the bold line in Fig. 3(a). On the other hand, the TOF spectrum Fig. 2 which depicts all (CN)₂ fragments reaching the detector, is fit by the kinetic energy distribution $P(E_T)$ indicated by the dashed line in Fig. 3(a). The discrepancy of the dashed and the solid $P(E_T)$ below ~80 kJ/mol is reminiscent of the findings for the OCCN fragment [see Fig. 3(b)]. It is therefore likely that this effect is due to the decay of slow (CN)₂ fragments which possess sufficient internal energy to dissociate spontaneously to CN+CN before reaching the detector (see below).

As mentioned above, the relative yield of the radical channel (1a) and the molecular channel (2) can be estimated from the relative signal intensities at m/e = 54 and 52, respectively. This estimate is now examined using the fit of the CO⁺ spectra in Fig. 6 by comparing the contribution from the molecular channel to that from the secondary decay of OCCN. The relative weight of the two contributions in Fig. 6 is ~1:3. With a fraction of 18% of nascent OCCN undergoing secondary decay, we obtain a branching ratio (radical channel)/(molecular channel) ≈ 17, consistent with the rough estimation given in Sec. III B. We believe the accuracy of this ratio to be within about 30%, which mainly results from the uncertainty in the fraction of the secondary dissociation of OCCN.

Photodissociation measurements with a polarized laser beam^{13,14} were carried out at m/e=26, 52, and 54. At all these mass settings the TOF spectra were found to be independent of the polarization angle and hence the fragment recoil anisotropy β is zero. In the TOF spectra of CO⁺ and CN⁺, the overlap of the components could potentially hide the anisotropy of fragments from a particular decay process but this is definitely not the case for $(CN)_2^+$ and OCCN⁺.

IV. DISCUSSION

Following excitation at 193 nm, $CO(CN)_2$ is found to dissociate into the products CN, CO, OCCN, and $(CN)_2$. Using the PTS method, the kinetic energy distributions of all these fragments could be measured and the analysis of this complete TOF data set is shown to be consistent with two distinct decay pathways. The major fraction $(94\% \pm 2\%)$ of the parent molecules decays via a radical channel to CN+OCCN (1a), while a small fraction $(6\% \pm 2\%)$ undergoes a molecular decay to $CO+(CN)_2$ (2). The excellent fit of all measured TOF spectra required no further primary processes, such as a three-body decay to CO+CN+CN, to be included in the reaction scheme. Thus based on these two primary decay channels we discuss the energetic and mechanistic features, including secondary decay processes, of the photofragmentation of $CO(CN)_2$.

A. Radical channel

The simplest decay involves a single C-C bond cleavage. The energy available to be partitioned among the primary photoproducts CN+OCCN following this reaction (1a) is given by

$$E_{\text{avl}}(\text{CN}+\text{OCCN}) = h\nu + E_{\text{int}}(\text{CO}(\text{CN})_2)$$
$$-D_0(\text{NC}-\text{COCN}). \tag{4}$$

The photon energy $h\nu$ is 619 kJ/mol and the internal energy $E_{\rm int}$ of CO(CN)₂ can be neglected owing to the efficient cooling in the supersonic expansion ($E_{\rm int} < 50 \, \text{K} \approx 0.4 \, \text{kJ/mol}$). The bond dissociation energy $D_0(\text{NC-COCN})$ has previously been estimated to be 430 kJ/mol¹ based on an *ab initio* calculation of the related molecule acetyl cyanide CH₃COCN.²⁷ Recent *ab initio* calculations carried out in our group showed that the elimination of -CN from CO(CN)₂ requires 20 kJ/mol less than the -CN elimination from CH₃COCN.²⁸ Therefore we now adopt 410 kJ/mol as the best estimate for $D_0(\text{NC-COCN})$, which yields $E_{\text{avl}} = 210 \, \text{kJ/mol}$. Experimentally, an upper bound for the bond dissociation energy is obtained from the high-energy threshold of the $P(E_T)$ fitted to the OCCN and CN spectra

$$D_0(\text{NC}-\text{COCN}) \le h\nu - E_T(\text{max}), \tag{5}$$

where the equality sign holds if all available energy is channeled into fragment recoil. The high-energy threshold in Fig. 3(b) of $E_T(\max) = 140 \pm 20 \text{ kJ/mol}$ yields $D_0(\text{NC}-\text{COCN})$ $\leq 480 \pm 20 \text{ kJ/mol.}$ Taking the true value as D_0 = 410 kJ/mol then even the internally coldest fragments have partitioned a substantial part of \approx 70 kJ/mol (\approx 33%) of the available energy into internal degrees of freedom. The uncertainty in $E_T(\max)$ is, however, relatively large due to the long flat tail of the $P(E_T)$ curve at high kinetic energies. The average kinetic energy of the fragment pair is $\langle E_T \rangle$ = 37 kJ/mol, which corresponds to an average internal energy $\langle E_{int} \rangle = E_{avl} - \langle E_T \rangle = 173 \text{ kJ/mol.}$ The latter being 82% of E_{avl} is quite large for a direct dissociation of a small molecule where the kinetic energy release is usually found to dominate the impulsive process. This would, however, be changed if one of the nascent fragment species is electronically excited. The only excited electronic state accessible in the range <210 kJ/mol is the $A^{2}\Pi$ state of CN lying 110 kJ/mol $(9245 \text{ cm}^{-1})^{29}$ above the ground state $X^2\Sigma$. Since the $P(E_T)$ distribution shows no discernible structure in this region, evidence for the formation of $CN(A^2\Pi)$ is lacking.

The internal energy deposited into OCCN can be substantial, in principle up to 210 kJ/mol if the CN counterfragment is formed with negligible internal (rovibrational and electronic) excitation. Thus a substantial part of nascent OCCN will have E_{int} exceeding the dissociation energy for the secondary decay of OCCN to CO+CN, which has been predicted to be 126 kJ/mol by an *ab initio* calculation.²⁷ Our experimental data are consistent with the partial decomposition of primary OCCN fragments as manifested by the fail-



FIG. 7. Energy level diagram of $CO(CN)_2$ and its possible photofragment species emerging from the molecular or the radical decay following excitation at 193 nm (619 kJ/mol).

ure to fit the OCCN signal and its counterfragment CN with the same $P(E_T)$ distribution after momentum-matching as shown in Fig. 3(b). The slow, internally hot OCCN fragments are missing in the OCCN spectra, which results in the truncated $P(E_T)$ displayed as dashed curve. Below a translational energy of $E_T \approx 50$ kJ/mol where this $P(E_T)$ starts to separate from the total $P(E_T)$ [marked by a thin line in Fig. 3(b)], the barrier to dissociation of OCCN is overcome and decomposition to CO+CN occurs. Although subject to a relatively large error, the bifurcation energy provides an upper limit for the barrier height given by E_{avl} $-E_T$ (bifurcation) ≈ 160 kJ/mol, which is consistent with the calculated dissociation energy of 126 kJ/mol.²⁷

B. Molecular channel

The photodissociation product detected at m/e = 52 can be assigned to one of three possible isomers of $(CN)_2$ emerging from reaction (2). While cyanogen (NCCN) and isocyanogen (CNCN) are well-known and stable species, diisocyanogen (CNNC) has not yet been observed and is predicted to be rather unstable.³⁰ The energies required to dissociate NCCN and CNCN to ${}^{2}\Sigma$ CN + ${}^{2}\Sigma$ CN are displayed in Fig. 7. The bond dissociation energy of NCCN has been determined experimentally from fragment Doppler profiles,³¹ while the value for D_0 (CNCN) was derived using the difference in stability from ab initio calculations of NCCN and $CNCN^{30}$ combined with $D_0(NCCN)$ from experiment. Obviously our mass spectroscopic detection does not allow a distinction between NCCN and CNCN,³⁰ but we believe that formation of NCCN is much more likely since NCCN is more stable than CNCN by about 134 kJ/mol and requires a much smaller conformational change along the reaction path (see below).

The generation of NCCN releases a large available energy of 638 kJ/mol owing to the exothermal formation of the strong new C–C bond $(D_0=555 \text{ kJ/mol},^{31} \text{ see Fig. 7})$. A remarkable feature of the $P(E_T)$ distribution found for the CO+NCCN pair is its high energy end being 170 \pm 15 kJ/mol below the maximum possible value $E_T(\max)$ indicated by the arrow [Fig. 3(a)]. This implies that the lowest internal energy (rovibrational and electronic) of the CO+NCCN pairs is $\approx 170 \text{ kJ/mol} (14200 \text{ cm}^{-1})$ or, in other words, that even the fragment pairs with the highest kinetic energy possess still such a substantial amount of internal energy. The average kinetic energy $\langle E_T \rangle$ of the CO+NCCN pair is 190±10 kJ/mol and corresponds to an average internal excitation of 430 kJ/mol (35 900 cm⁻¹). The only excited state accessible within $E_{avl} = 638 \text{ kJ/mol}$ is the $\tilde{a}^{3}\Sigma$ state of NCCN at 395 kJ/mol³² which would require intersystem crossing to occur. Since a partial production of such a species would lead to an additional $P(E_T)$, structure in the distribution curve of Fig. 3(a) should become discernible, which is, however, not evident. The $P(E_T)$ in Fig. 3(a) shows a bifurcation at $E_T \sim 80 \text{ kJ/mol}$ where the fragment pairs have acquired an internal energy $(E_{avl} - E_T)$ of 560 ± 20 kJ/mol. This value is close to $D_0(NC-CN) = 555 \text{ kJ/mol}$, in support of our suggestion that at $E_T < 80 \text{ kJ/mol}$ the nascent NCCN product can decay spontaneously into CN+CN.

Finally, we briefly address the one-step (synchronous or decay^{11,12} asynchronous concerted) three-body to CO+CN+CN (3) which is also energetically feasible at 193 nm. The available energy is, however, merely ~ 80 kJ/mol (Fig. 7). The average kinetic energy $\langle E_T \rangle = E_{avl} - \langle E_{int} \rangle$ of each fragment is therefore expected to be below 20 kJ/mol. Examination of the $P(E_T)$ curves for CN⁺ and CO⁺ at the corresponding low energy side in Fig. 3 reveals that a possible contribution from such a decay would be small. Moreover, since the analysis of the experimental data set was very satisfactory without inclusion of an additional decay mode, a one-step three-body decay can be considered negligible under our excitation condition.

C. Mechanistic considerations

Excitation at 193 nm is assumed to prepare the 3s Rydberg state of CO(CN)₂. This state has B_2 symmetry in C_{2v} , which implies a transition dipole moment for the $B_2 \leftarrow A_1$ transition lying in the molecular plane perpendicular to the C=O bond.^{19,21} In the case of the radical decay (1a) with an instantaneous separation of the fragments OCCN and CN and with a recoil direction of CN along the breaking C-C bond, an anisotropy $\beta = 1.25$ is expected.³³ The angle \angle (CN-C-CN)~120° is taken from the geometry of the molecule in the ground state.³⁴ On the other hand, for the molecular decay involving a collinear recoil of CO and NCCN, one would expect $\beta = -1.0$ if the decay again is instantaneous, i.e., within a time much shorter than a rotational period of the parent molecule.³³ The lack of any anisotropy ($\beta = 0 \pm 0.1$) on the fragments of the two channels may therefore indicate that the two decay processes are relatively slow (≥ 1 ps) or the initially excited potential surface is deactivated by, e.g., internal conversion, to the dissociative ground state surface losing the initial alignment. Since in contrast to the initial B_2 state, the A_1 ground state is described by a wave function without a nodal plane between the two CN groups, this state would satisfy the requirement for the molecular decay path proceeding over a transition state under retention of the C_{2v} symmetry. While the two old C-C bonds are elongated, the new C-C bond between the two cyano groups is formed. Considering the substantial change in the distance between the two cyano C atoms [from 256 pm^{34} in CO(CN)₂ to 139 pm^{35} in NCCN], the excitation of the C-C stretching mode in the nascent NCCN product is expected to be high, as well as the excitation of the cisbending mode (233 cm^{-1}) due to the simultaneous change from the bent to the linear geometry. This expectation is supported by the large measured average internal energy of 430 kJ/mol which also indicates a high-lying transition state in agreement with results from a preliminary ab initio calculation.²⁸ On the other hand, a distortion of the initially excited molecule along the reaction path resulting in a break of the C_{2n} symmetry, such as by an asymmetric C-CN stretching motion, will preferentially create the product CN+OCCN. The radical channel which strongly dominates the decay is somewhat surprisingly also characterized by a large internal energy release. A prior distribution predicts a fragment partitioning of 14% into translation and 86% into internal energy; this is indeed close to the observed partitioning of $\langle E_T \rangle = 18\%$ and $\langle E_{int} \rangle = 82\%$. In view of this partitioning, an exit channel barrier in the direct C-C fission seems likely, which would then suggest that the formation of OCCN+CN proceeds via an intermediate state, such as the $(n\pi^*)$ or even $(n\pi^*)$ state, rather than the ground state, in analogy to the mechanisms proposed for other carbonyl compounds.^{21,36,37} In conclusion, the absence of fragment anisotropy and an energy partitioning conforming to a statistical distribution is consistent with a relatively slow and indirect dissociation process (1a), and similar findings suggest the same features for the molecular decay (2), which involves, in addition, a rather complex transition state.

V. CONCLUSIONS

The collision-free, photoinduced decay of $CO(CN)_2$ at 193 nm (~620 kJ/mol) has been investigated using photofragment translational energy spectroscopy. We monitored the TOF distributions of the photofragments CO, CN, OCCN, and NCCN. Excellent agreement with the complete set of spectra measured at different masses and scattering angles was obtained with the following scheme of decay pathways.

The radical channel (1a) with a yield of $94\% \pm 2\%$ produces the primary dissociation products CN+OCCN with the average internal energy (82%) strongly exceeding the translation energy (18%). A fraction of $18\% \pm 6\%$ of the OCCN radicals possesses sufficient internal energy to undergo secondary decay to CO+CN over a barrier of approximately ≤ 160 kJ/mol. The low average kinetic energy of the primary products, together with an isotropic recoil distribution of the fragments OCCN and CN, indicate that the dissociation mechanism is indirect and slow on a time scale of a parent rotation.

The molecular decay channel (2) produces the fragments $CO+(CN)_2$ with a yield of $6\% \pm 2\%$. This is, to our knowledge, the first observation of a photoinduced unimolecular decay which involves the cleavage of two bonds and the formation of a new combination product with more than two atoms. From the isotropic recoil distribution of $(CN)_2$ we conclude that this decay process is slow relative to the parent rotation, not unexpected in view of the complex transition state involved. The fragment species $(CN)_2$ is assigned to cyanogen (NCCN) rather than isocyanogen (CNCN) based on mechanistic and energetic arguments. The fragments CO+NCCN have an excess energy of 638 kJ/mol, essentially the equivalent of the deposited photon energy, owing to the strongly exothermal formation of a new C-C bond. The substantial change of bond angles and lengths during bond breaking and bond formation is probably responsible for the fact that an average fraction of 70% of this excess energy is partitioned as internal excitation to the fragments, and that the internal energy distribution allows a small part $(\sim 7\%)$ of nascent NCCN to dissociate into CN+CN. Since our experimental findings are consistent with the molecular decay proceeding on the ground state potential surface, ab initio calculations appear promising to determine the geometry of $CO(CN)_2$ at the transition state and to further elucidate the dynamics of the molecular decay path.

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