

## Selective dissociation of the stronger bond in HCN using an optical centrifuge

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Using the example of the HCN molecule, we study theoretically the possibility of selectively breaking the stronger bond in a triatomic molecule by rotationally accelerating it in an optical centrifuge using a combination of two oppositely chirped and counter-rotating strong laser fields. In our simulation the resultant field forces rotational acceleration of the HCN molecule to a point where the centrifugal force between the two heavy atoms (C and N) exceeds the strength of their (triple) bond. The effects of bending, rovibrational coupling, and the Coriolis force, which conspire to prevent the molecule from rotational dissociation into HC+N, can be efficiently counteracted by simple optimization of the frequency chirp. © 2002 American Institute of Physics. [DOI: 10.1063/1.1478696]

The dipole moment induced in a molecule by a laser field depends on the orientation of the molecule with respect to the laser polarization vector. In turn, interaction of the induced dipole with the same laser field creates an angle-dependent potential that tends to align the molecule along the laser polarization direction.<sup>1,2</sup> In the simplest case of a linearly polarized far off-resonant field with intensity  $I_0$  and a linear molecule with parallel and perpendicular polarizability tensor components  $\alpha_{\parallel}$  and  $\alpha_{\perp}$ , the effective potential is  $U_0 \cos^2 \theta$ , where  $\theta$  is the angle between the molecular axis and the polarization vector, and the well depth  $U_0 = (\alpha_{\parallel} - \alpha_{\perp})I_0/4$ . Typically, in diatomic molecules such as  $\text{Cl}_2$ ,  $\text{I}_2$ ,  $\text{N}_2$ , a well-depth of a few tens of meV can be created and sustained for tens of picoseconds using infrared radiation,<sup>3,4</sup> without ionizing the molecule. This well depth can exceed room temperature ( $kT \approx 25$  meV), and give rise to efficient alignment of rotationally hot molecules.

For a molecule with three different polarizability tensor components, an elliptically polarized field has been used to align the molecule in three dimensions.<sup>5</sup> Molecular alignment has also been used to control simple unimolecular reactions triggered by either parallel or perpendicular transitions;<sup>6,7</sup> the efficiency of the parallel vs the perpendicular transition is controlled by aligning the molecule.

The same basic physics can be used to force molecular rotation<sup>8,10</sup> in the so-called “optical centrifuge,” as was demonstrated experimentally in Ref. 11 for the diatomic molecule  $\text{Cl}_2$ . In that experiment  $\text{Cl}_2$  was rotationally accelerated to reach angular momentum states  $J > 400$  until the centrifugal force broke the bond. The centrifuge involves using a linearly polarized laser field whose polarization vector is slowly rotated. A molecule aligned with the field follows this rotation, and controlled rotational acceleration is forced by accelerating the rotation of the polarization vector.<sup>8</sup> Such a laser field has the form,

$$\mathcal{E} = \mathcal{E}_0 f(t) \cos(\omega_L t) [\mathbf{x} \cos(\phi_L(t)) + \mathbf{y} \sin(\phi_L(t))], \quad (1)$$

where  $\omega_L$  is the carrier frequency,  $\phi_L(t)$  defines the direction

of polarization, and  $f(t)$  is the pulse envelope. The centrifuge is created<sup>8</sup> by combining two circularly polarized, counter-rotating fields with slightly different frequencies  $\omega_{\pm} = \omega_L \pm \Omega$ . In this case the polarization vector rotates with the frequency  $d\phi_L(t)/dt = \Omega$ . Rotational acceleration is achieved by chirping the frequencies of the two fields in opposite directions. For example, setting  $\hbar\Omega = \beta t$  (a linear chirp) gives a constant rotational acceleration.

Here we show by numerical simulation that selective rotational dissociation of a strong bond between heavy nuclei can be achieved in a triatomic molecule. An important aspect of rotational dissociation in the optical centrifuge is minimal mixing between rotational and vibrational degrees of freedom during rotational acceleration. Dissociation is achieved by slowly modifying the effective potential energy surface; the smoothly increasing centrifugal force gently stretches the bonds. Since the centrifugal force is greater between heavier nuclei, this opens the possibility of selectively breaking a stronger bond when such a bond is between heavier nuclei.

For illustration, we take a rather extreme example, HCN, in which there is a strong and a weak bond. The HCN molecule has bond strengths  $D_{\text{CN}} = 10.6$  eV and  $D_{\text{CH}} = 5.7$  eV. The possibility to use strong laser fields in combination with optimal control approach to break the stronger bond in HCN has been studied theoretically in Ref. 12 (for a linear model and assuming an aligned molecule), while strong-field controlled isomerization in HCN using mid-infrared fields has been theoretically addressed in Ref. 13. For the centrifuge, we assume that the carrier wavelength is  $\lambda = 800$  nm, that the available coherent bandwidth corresponds to a 6 fs transform-limited pulse, and that the two counter-chirped, counter-rotating fields are obtained from the red and blue halves of the pulse spectrum, similar to the experiment in Ref. 11. The angular frequency needed to break the CN bond by the centrifugal force is  $\Omega_D = 1.24 \times 10^{14} \text{ s}^{-1}$  (20 THz) within the limits of the coherent bandwidth  $\Delta\omega = 72$  THz of the 6 fs pulse.

We are especially interested in the role of bending and of

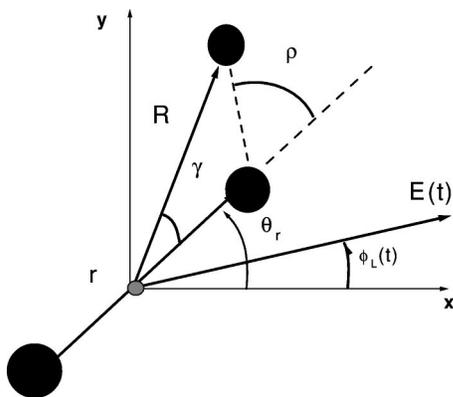


FIG. 1. The coordinates used for HCN. The origin is the center-of-mass of the CN moiety,  $r$  is the length of CN,  $R$  is the distance between the H-atom and the center-of-mass of the CN moiety, and  $\gamma$  is the Jacobi bending angle.  $\theta(t) = \theta_r - \phi_L(t)$  defines the angle between the CN bond and the laser field.

the Coriolis coupling between vibration and rotation. Is it possible to deposit over 11 eV of rotational energy into the CN bond without a rapid energy redistribution into other modes? By simulating the HCN dynamics on the ground electronic surface in the presence of the field given in Eq. (1), we show that simple optimization of the  $\Omega(t)$  chirp is sufficient to suppress effects competing with rotational dissociation.

The geometry of the molecule is shown in Fig. 1, where we define the Jacobi coordinates used in our model. The centrifuge field is rotating in the  $xy$ -plane and  $\phi_L$  determines the direction of the polarization vector of the centrifuge field. We assume that the molecule is confined to the  $xy$ -plane, and in this plane  $\theta_r$  determines the orientation of the CN bond. This planar approximation has been verified numerically<sup>8,9</sup> and is justified by the fact that the centrifuge field simultaneously increases  $J$  and  $J_z$ ,<sup>8,9</sup> so that the rotationally accelerating molecule rotates in states with  $J \approx J_z \gg 1$ .

Four degrees of freedom are included in our numerical description. We include the rotational mode described by the angle  $\theta_r$  and its conjugate (angular) momentum  $J \equiv p_{\theta_r}$ , and the coordinates and momenta that describe the three vibrations ( $r$ ,  $p_r$ ,  $R$ ,  $p_R$ ,  $\gamma$ , and  $p_\gamma$ ). The classical Hamiltonian is

$$H = \frac{p_r^2}{2\mu_{\text{CN}}} + \frac{p_R^2}{2\mu_{\text{HCN}}} + \frac{p_\gamma^2}{2} \left[ \frac{1}{\mu_{\text{CN}} r^2} + \frac{1}{\mu_{\text{HCN}} R^2} \right] + \frac{J^2}{2\mu_{\text{HCN}} r^2} - \frac{J \cdot p_\gamma}{\mu_{\text{CN}} r^2} + V + V_{\text{int}}, \quad (2)$$

where

$$\mu_{\text{CN}} = \frac{m_{\text{C}} \cdot m_{\text{N}}}{m_{\text{C}} + m_{\text{N}}}, \quad \mu_{\text{HCN}} = \frac{m_{\text{H}}(m_{\text{C}} + m_{\text{N}})}{m_{\text{C}} + m_{\text{N}} + m_{\text{H}}}, \quad (3)$$

$V(r, R, \gamma)$  is the field-free potential energy surface of HCN, and  $V_{\text{int}}(r, R, \gamma, \theta_r, t)$  is the interaction potential. The potentials  $V$  and  $V_{\text{int}}$  are initially set up analytically using the coordinates  $r_{\text{CN}}$ ,  $r_{\text{CH}}$ , and  $\rho$ , where  $\rho$  (see Fig. 1) is the supplement of the HCN bond angle  $\alpha$ , i.e.,  $\rho = \pi - \alpha$ ; transformation to Jacobi coordinates is made later.

The potential energy surface  $V(r_{\text{CN}}, r_{\text{CH}}, \rho)$  has to allow for bending and for the stretching of the bonds to dissociation.

TABLE I. The potential surface parameter values  $Y_{jkm}$  and their standard errors (in eV) for the ground state of HCN [see Eq. (4)].

$j$	$k$	$m$	$Y_{jkm}$	Std. error	$j$	$k$	$m$	$Y_{jkm}$	Std. error
0	0	2	5.13	0.21	2	1	3	-14.99	4.16
0	0	3	-3.24	0.21	3	0	2	-6.35	0.59
0	1	1	3.25	1.11	3	0	3	-5.67	0.60
0	1	3	-35.10	7.23	0	4	0	2.89	0.43
0	1	4	30.12	6.16	0	4	2	-2.72	0.91
1	0	3	-1.26	0.10	1	3	0	1.48	0.23
0	2	0	13.46	0.13	2	2	0	3.57	0.40
0	2	1	-1.71	0.40	2	2	1	-3.61	0.55
0	2	3	1.92	0.43	3	1	0	1.06	0.29
1	1	0	-0.92	0.18	4	0	0	4.62	0.73
2	0	0	6.41	0.18	0	5	0	-5.70	0.33
0	3	1	-6.63	2.01	0	5	1	3.25	0.81
0	3	2	19.82	5.09	1	4	1	-11.33	1.41
0	3	3	-14.02	3.34	1	4	2	8.25	1.41
1	2	1	6.55	2.23	2	3	0	-2.58	0.36
1	2	2	-15.38	5.75	2	3	1	2.87	0.67
1	2	3	11.68	3.82	3	2	0	-5.03	0.40
2	1	0	-0.73	0.20	3	2	1	-11.96	1.80
2	1	1	-7.15	2.26	3	2	2	-9.90	1.75
2	1	2	22.82	6.31	5	0	0	-5.25	0.58

We have obtained it in a simple analytical form using the internally contracted multireference configuration interaction (MRCI) *ab initio* method<sup>14</sup> with the MOLPRO program system.<sup>15</sup> The range of the HCN bond angle  $\alpha$  was restricted to be from  $180^\circ$  to  $90^\circ$ , based on preliminary simulations of the importance of bending which showed that larger bending did not occur prior to dissociation, and hence that HCN-CN isomerization need not be considered. The calculations involved 362 geometries with  $0.9 \text{ \AA} \leq r_{\text{CN}} \leq 3.5 \text{ \AA}$ ,  $0.8 \text{ \AA} \leq r_{\text{CH}} \leq 3.5 \text{ \AA}$ , and  $90^\circ \leq \alpha \leq 180^\circ$ . The points covered an energy range of about 14 eV. The correlation-consistent polarized valence quadruple-zeta (cc-pVQZ) basis sets of Dunning<sup>16</sup> were used. The orbital basis sets for carbon and nitrogen consisted of  $(12s \ 6p \ 3d \ 2f \ 1g)$  contracted to  $[5s \ 4p \ 3d \ 2f]$ , and for hydrogen of  $(6s \ 3p \ 2d \ 1f)$  contracted to  $[4s \ 3p \ 2d]$ . Multiconfiguration self-consistent field (MCSCF) calculations<sup>17</sup> were used to define the orbitals for the MRCI. The reference wave function was a complete expansion in those orbitals which correlate with atomic valence orbitals. The calculations were performed in  $C_s$  symmetry with orbitals  $3a'$  to  $9a'$  and  $1a''$  to  $2a''$  in the active space. The carbon and nitrogen  $1s$  orbitals were not correlated, but were optimized at the MCSCF level. The optimized geometry obtained was linear with  $r_{\text{CH}}^e = 1.061 \text{ \AA}$  and  $r_{\text{CN}}^e = 1.158 \text{ \AA}$  (compared to experimental values of  $1.0655 \text{ \AA}$  and  $1.1532 \text{ \AA}$  respectively<sup>18</sup>).

The analytical three-dimensional function  $V$  that was fitted through the points is a slight extension of that originally introduced in Ref. 19 (see also Ref. 20),

$$V(r_{\text{CN}}, r_{\text{CH}}, \rho) = \sum_{jkm} Y_{jkm} y_1^j y_2^k y_3^m (1 - \cos \rho)^m, \quad (4)$$

where  $y_i = 1 - \exp(-a_i \Delta r_i)$ ,  $\Delta r_i = r_i - r_i^e$  ( $r_i^e$  is the equilibrium value),  $r_1 = r_{\text{CH}}$ ,  $r_3 = r_{\text{CN}}$ ,  $a_1 = 1.6 \text{ \AA}^{-1}$ ,  $a_3 = 2.0 \text{ \AA}^{-1}$ , and the  $Y_{jkm}$  are adjustable parameters. We could usefully vary 40 parameters, and their values and standard errors are given in Table I; the standard deviation of the

fitting was 0.093 eV. For linear HCN the potential extrapolates to dissociation of the CH and CN bonds with energies  $D_{\text{CH}}=5.77(5.66)$  eV and  $D_{\text{CN}}=10.69(10.63)$  eV, where the experimentally derived values<sup>21,22</sup> are in parentheses. The standard deviation and the errors of the extrapolations to dissociation indicate that  $V$  is sufficiently precise for our purposes.

To obtain an expression for the interaction potential of HCN in the laser field of Eq. (1) we write the polarizability of HCN as the sum of CH and CN bond polarizabilities. The parallel and perpendicular components of the dynamic HCN polarizability at  $\lambda=800$  nm are approximated by their static values; the equilibrium values and their (linear) dependence on the bond lengths are taken from Refs. 23, 24. In  $\text{\AA}^3$  we write

$$(\alpha_{\parallel}^{\text{CH}} - \alpha_{\perp}^{\text{CH}}) = (0.651 + 0.873(r_{\text{CH}} - r_{\text{CH}}^e)) \times (1 - \tanh(r_{\text{CH}}/r_{\text{CH}}^e - 4))/2, \quad (5)$$

and

$$(\alpha_{\parallel}^{\text{CN}} - \alpha_{\perp}^{\text{CN}}) = (1.175 + 1.937(r_{\text{CN}} - r_{\text{CN}}^e)) \times (1 - \tanh(r_{\text{CN}}/r_{\text{CN}}^e - 4))/2, \quad (6)$$

where the bond lengths are in  $\text{\AA}$ , and the tanh term is used to avoid divergence of the polarizability for  $r_i$  values outside the range of interest. For each bond we define  $U_i(r_i, t) = (\alpha_{\parallel}^i - \alpha_{\perp}^i)I_0(t)/4$ , where  $i$  refers to CH or CN. Using these expressions we obtain

$$V_{\text{int}}(r_{\text{CN}}, r_{\text{CH}}, \rho, \theta, t) = U_{\text{CN}}(r_{\text{CN}}, t)\cos^2(\theta(t)) + U_{\text{CH}}(r_{\text{CH}}, t)\cos^2(\theta(t) + \rho), \quad (7)$$

where  $\theta(t) = (\theta_r - \phi_L(t))$  is the angle between the CN bond and the polarization vector of the laser field. At intensity  $I_0 = 2 \times 10^{13}$  W/cm<sup>2</sup> this gives a well depth of  $U_0 \approx 50$  meV at the equilibrium geometry.

In this numerical study we solve Hamilton's canonical equations of motion using the fourth-order Runge-Kutta method<sup>25</sup> for an ensemble of initial conditions corresponding to random orientations of the HCN molecule at its equilibrium geometry. We set random values of  $\theta_r$ , with the initial angular momentum  $J=0$ . In this classical calculation the initial conditions include the zero-point bending energy and the corresponding distribution of  $\gamma$ , but the bond lengths are taken to be fixed at their equilibrium values.

At  $t=0$ , we turn the laser field [Eq. (1)] on and keep the intensity  $I_0$  constant. Our goal is to find the range of pulse parameters that will result in efficient dissociation of the triple bond within a 50 ps pulse duration. Significantly longer pulses require more energy, and a 50 ps pulse at intensity  $I_0 \sim 10^{13}$  W/cm<sup>2</sup> is experimentally feasible.<sup>11</sup> For the entire calculation we set  $I_0 = 2.0 \times 10^{13}$  W/cm<sup>2</sup>, which corresponds to a negligible ion signal of about  $2.5 \times 10^{-4}$ . This value was estimated by adjusting the value determined in Ref. 26 for Kr to the value appropriate for a 50 ps laser pulse. The Kr atom has an ionization potential of 14 eV which is close to that of HCN (13.9 eV). Note that the same

intensity was used in the experiment with  $\text{Cl}_2$ ,<sup>11</sup> which has a lower ionization potential of 11.5 eV, and there was negligible ionization.

First, we assume that the polarization vector rotates with constant acceleration  $\beta$ , i.e.,  $\phi_L(t) = \beta t^2/2$  and  $\Omega(t) = \beta t$ . The angular frequency at which rotational dissociation of HCN into HC+N begins is  $\Omega_D = 1.24 \times 10^{14}$  s<sup>-1</sup>, and setting  $\beta = 3 \times 10^{-9}$   $E_{\text{h}}t_0^{-1}$  ( $3.4 \times 10^9$  eV s<sup>-1</sup>) we reach this frequency in about 24 ps. The maximum value of  $\beta$  is restricted by the characteristic gradient of the angular well  $\sim U_0/\pi$  and the HCN moment of inertia  $I_{\text{HCN}}$  (Ref. 8) to be  $\beta_{\text{max}} \sim U_0/(\pi I_{\text{HCN}}) \sim 10^{-8}$   $E_{\text{h}}t_0^{-1}$ .

A typical trajectory is shown in Fig. 2. Angular trapping is described by the angle  $\theta(t)$ . Up until  $t \approx 22$  ps the angle  $\theta$  is close to 0 and the molecule is trapped so that it follows the rotation of the angular trap. During this time interval the bending amplitude decreases since the molecule is stiffened against bending by the rotation. Both bonds are progressively stretched by the centrifugal force, with virtually no vibrational excitation or energy exchange between them. As expected, the stronger CN bond is significantly more stretched than the CH bond ( $r_{\text{CN}}/r_{\text{CN}}^e \approx 1.35$ , whereas  $r_{\text{CH}}/r_{\text{CH}}^e \approx 1.1$ ).

When the CN bond starts to break after about 22 ps, the molecule is rapidly ejected from the rotating angular trap by the Coriolis force [see the rapid change in  $\theta(t)$  in Fig. 2], which is similar to the situation for a diatomic molecule.<sup>8</sup> The bonds are no longer steadily pulled by the increasing centrifugal force and begin to vibrate and exchange energy. During this time, the centrifuge continues its rotation, and gives an accelerated series of kicks to the molecule each time  $\theta(t)/\pi$  is an integer. These kicks eventually lead to dissociation of either bond at much later times, with CN bond breaking in about 60% of the cases after the molecule is ejected from the centrifuge (see Fig. 2 where the CN bond breaks at around  $t=70$  ps). Statistically, 25% of the cases result in direct fast dissociation of the CN bond by the centrifugal force, while in 75% cases the molecule is ejected from the trap before the strong bond is broken. If the laser pulse is kept on for sufficiently long time, the strong CN bond still dissociates in 60% of those cases.

The physics behind the ejection and the approach to counteracting it can be understood classically and quantum mechanically. Let  $R(J)$  and  $r(J)$  be the equilibrium values taking into account bond stretching by the centrifugal force. The corresponding moment of inertia is  $I_{\text{HCN}}(J) = \mu_{\text{HCN}}R^2(J) + \mu_{\text{CN}}r^2(J)$ . The adiabatic following of the trap rotation by the molecule implies that its angular momentum is  $J = I_{\text{HCN}}(J)\Omega(t)$ .<sup>8</sup> Rewritten in the form  $J/I_{\text{HCN}}(J) = \Omega(t)$ , this equation can also be understood quantum-mechanically as a resonance between the rotational spacing and the driving frequency  $\Omega$ .

For linear angular acceleration  $\Omega(t) = \beta t$  the resonance is lost when the rotational spacing starts to decrease with  $J$  while  $\Omega(t)$  continues to increase, leading to the loss of the molecule from the angular trap. Decrease of  $\Omega(J) = J/I_{\text{HCN}}(J)$  is exactly what happens just before rotational dissociation; the function  $\Omega(J) = J/I_{\text{HCN}}(J)$  reaches its maximum  $\Omega_C$  when the angular momentum  $J = J_C$  is less than that required for dissociation,  $J_D$ .<sup>8</sup> The rotational fre-

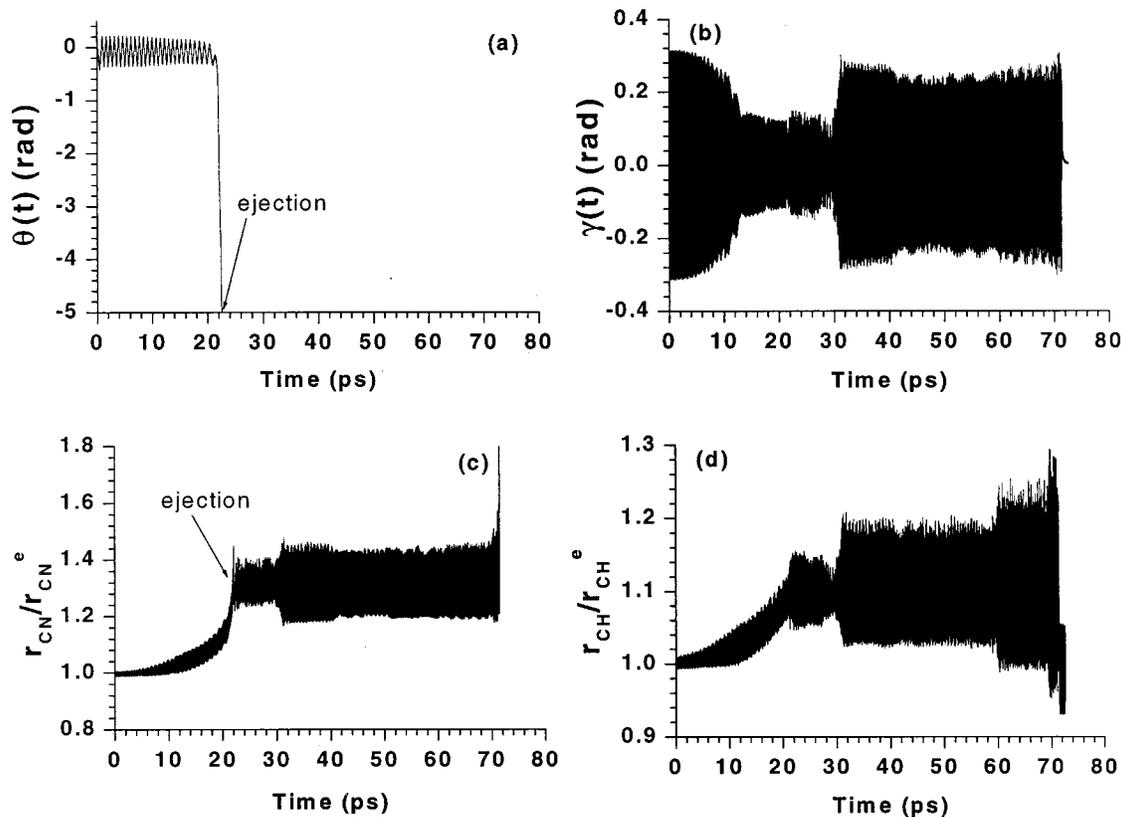


FIG. 2. A typical trajectory when the polarization vector rotates with the constant acceleration  $\beta = 3 \times 10^{-9} E_h t_0$ . The molecule is ejected from the trap after about 22 ps, and the CN bond eventually breaks after about 70 ps.

quency required for dissociation,  $\Omega_D = J_D / I_{\text{HCN}}(J_D)$  is less than  $\Omega_C$ .

To keep a molecule in the angular trap one should try to maintain the resonance  $J / I_{\text{HCN}}(J) = \Omega(t)$  as long as possible in the vicinity of  $J_C$ . One possibility is to follow  $\Omega(J)$ , first increasing  $\Omega(t)$  up to  $\Omega_C$  and then decreasing it. But a much simpler solution turns out to be sufficient.

We consider the function  $\Omega(t)$  which grows linearly as  $\beta t$  when  $\Omega \ll \Omega_C, \Omega_D$ , but then saturates at  $\Omega_0 \approx \Omega_D, \Omega_C$ . Numerically, we model this function as

$$\Omega(t) = \Omega_0 * \tanh\left(\frac{\beta t}{\hbar \Omega_0}\right), \quad (8)$$

where  $\Omega_0$  is the optimization parameter. Setting  $\Omega_0 = 1.12 \times 10^{14} \text{ s}^{-1}$  and  $\beta = 3.4 \times 10^9 \text{ eV s}^{-1}$ , we obtain a dramatic improvement in the selective rotational dissociation. A typical trajectory is shown in Fig. 3. Both bonds are steadily stretched until the centrifugal force breaks the triple CN bond, and only at this point is the molecule ejected from the angular trap. Similar results are obtained in a model calculation with HCN kept linear. This shows that the dissociation dynamics are not affected by the bending motion.

With these laser characteristics, which are similar to those used with  $\text{Cl}_2$ ,<sup>11</sup> 98% of trajectories lead to successful dissociation of the CN bond by the centrifugal force, provided the molecule is caught by the centrifuge during the turn-on. Overall 73% of trajectories lead to dissociation of the CN bond while 25.6% of trajectories are not trapped by the centrifuge. The remaining, 1.4%, correspond to dissocia-

tion of the CH bond or premature loss of molecule from the rotating angular trap. The average time of dissociation for this chirp rate is 55 ps.

The dissociation time can be decreased by using higher values of  $\beta$ . The turn-on time  $t_{\text{on}}$  is also decreased,  $I_{\text{HCN}}(\beta t_{\text{on}})^2 < U_{\text{HCN}}$ . For  $\beta = 5 \times 10^{-9} E_h t_0^{-1}$ , 68.5% of trajectories correspond to the molecule being trapped by the centrifuge field. For these trajectories only 3% are ejected earlier, and the rest of the trajectories (97%) lead to a selective dissociation of the CN bond (we do not observe CH dissociation) at  $t \approx 33$  ps. For  $\beta = 7 \times 10^{-9} E_h t_0^{-1}$  the same percentage of molecules is dissociated but with an average dissociation time equal to 24 ps.

The optimization is rather sensitive to the value of  $\Omega_0$ . Too low a value is insufficient for dissociation, while too high a value leads to premature ejection of the molecule from the trap. To show this a calculation was done with  $\beta = 5 \times 10^{-9} E_h t_0^{-1}$  and  $\Omega_C = 0.0026 t_0^{-1}$  ( $1.07 \times 10^{14} \text{ s}^{-1}$ ). As the number of trapped molecules only depends on the value of  $\beta$ , we obtain the same rate as previously (68.5%). But, in this case, none of the trapped molecule are dissociated because the angular velocity of the laser is not high enough for the dissociation angular momentum  $J_D$  to be reached. When  $\Omega_C$  is increased to  $0.0028 t_0^{-1}$ , we still observe only the dissociation of the CN bond, but with a lower overall efficiency (89.25% instead of 97%). However the average time for dissociation is decreased. For example  $\Omega_C = 0.0027 t_0^{-1}$  leads to  $t \approx 33$  ps, whereas  $\Omega_C = 0.0028 t_0^{-1}$  leads to  $t \approx 26$  ps.

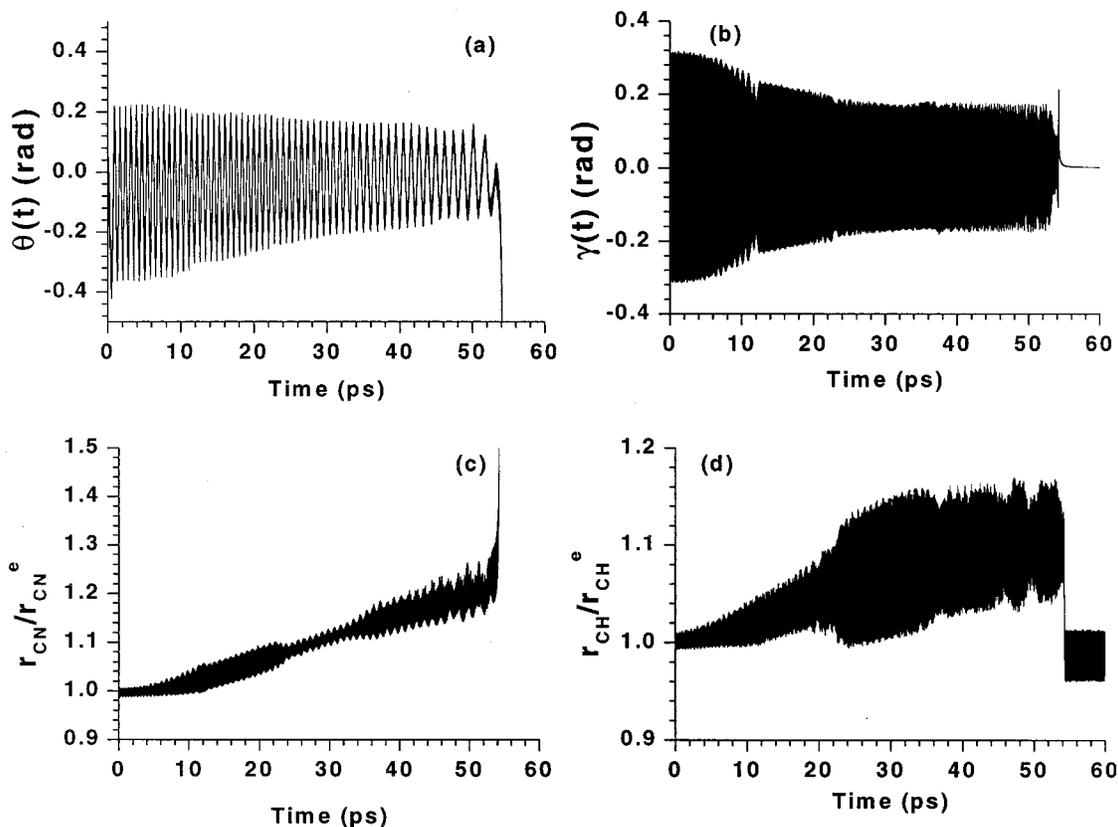


FIG. 3. A typical trajectory obtained with the polarization vector rotating according to the expression given in Eq. (8) with  $\Omega_0 = 1.12 \times 10^{14} \text{ s}^{-1}$  and  $\beta = 3.4 \times 10^9 \text{ eV s}^{-1}$ . Both bonds are steadily stretched until the centrifugal force breaks the CN bond, and only at this point is the molecule ejected from the trap. Bending is suppressed during rotational acceleration.

In conclusion, we have demonstrated that selective dissociation of the much stronger CN bond in the linear triatomic molecule HCN is possible using the optical centrifuge. The bending of the molecule during rotational acceleration is not significant. The most important effect competing with rotational dissociation is the ejection of the molecule from the angular trap due to the Coriolis force, and this is very similar to the situation for a diatomic molecule.<sup>8,10</sup> It can be effectively counteracted by a simple optimization of the angular acceleration, and this can be easily understood both classically and quantum-mechanically. As a result, it is possible to deposit over 11 eV of rotational energy into the CN bond, without losing it to the other degrees of freedom, by using laser parameters well within the reach of current femtosecond technology; the coherent bandwidth required for rotational dissociation of HCN into HC+N is well within the limits of a 6 fs pulse.

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