Vibration facilitated roaming in the isomerization of CO adsorbed on NaCl: A quasiclassical simulation based on cluster models

Apurba Nandi[1], **Peng Zhang**[2], **Jun Chen**[3], **Hua Guo**[3], **and Joel M. Bowman**[1,*]

[1]Department of Chemistry and Cherry L. Emerson Center for Scientific Computation, Emory University, Atlanta, Georgia 30322, U.S.A.
[2]Department of Chemistry, Duke University, Durham, North Carolina 27708, U.S.A.
[3]Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico 87131, U.S.A.
[*]Corresponding author: jmbowma@emory.edu

ABSTRACT

The desire to better understand the quantum nature of isomerization led to recent experimental observations of the vibrationally induced isomerization of OC–NaCl(100) (‘C-down’) to CO–NaCl(100) (‘O-down’). Here we investigate the mechanism of this isomerization by performing dynamics calculations using finite $(\text{CO–NaCl})_n$ cluster models. We construct new potential energy surfaces (PESs) for CO–NaCl and CO–CO interactions using high-level *ab initio* data and report key properties of the bare CO–NaCl PES, which show much in common with the experiment. We investigate the isomerization dynamics using several cluster models and, in all cases, isomerization is seen for highly excited CO vibrational states, in agreement with experiment. A detailed examination of the reaction trajectories indicates that isomerization occurs when the distance between CO and NaCl is larger than the distance at the conventional isomerization saddle point, which is a strong indicator of ‘roaming’.

Introduction

Isomerization is a pervasive phenomenon in chemistry and yet it has rarely been observed in real time experimentally. Theoretical work has been extensive on this topic; however, few quantum dynamical studies of isomerization have been reported. The isomerization of HCN to HNC is one notable exception, where isomerizing quantum states were reported using an accurate potential.[1,2] Another example is isomerization between acetylene and vinylidene, where theory was able to assign vibrational features in photodetachment of vinylidene anion.[3,4]

Recent experiments reported isomerization of CO adsorbed on NaCl(100)[5] (flipped to OC) for highly excited vibrational states of CO.[6] By resolving small differences in the emission spectra of CO and OC adsorbed on the surface the authors conclusively observed the isomerization from “C-down” to “O-down” on the surface. This experiment is a major step in observing isomerization dynamically, under state-controlled conditions in a condensed phase environment. The mechanism for this isomerization is complex as it involves excitation of the CO to high vibrational states via CO-CO energy pooling, followed by isomerization, subsequent emission and perhaps (partial) stabilization of the O-down isomer.

Several aspects of the experiment are important for theoretical modeling. First, it was determined that in the energetically favored C-down orientation[7] the CO bond axis makes an angle of approximately 25 deg relative to the surface normal.[5,7] For the O-down isomer that angle is approximately 45 deg.[5]

Second, the fundamental CO frequency, of the C-down isomer is blue-shifted by 7.6 cm ^{1}, whereas the O-down isomer fundamental is red-shifted by 9.3, cm ^{1}, relative to free CO.[5] Third, isomerization is only observed for the C-down isomer for CO for vibrational greater than roughly 20. And fourth the O-down isomer is also highly vibrationally excited, as evidenced by the overtone emission spectrum of that isomer.

In this Report we present a dynamics study of CO isomerization on the NaCl(100) surface by modeling the system ~~by~~ a finite CO-NaCl cluster. We develop a potential energy surface (PES) for the cluster that consists of a new *ab initio* CO-NaCl PES (for rigid NaCl) and a re-fit, using permutationally invariant polynomials (PIPs) to high-level *ab initio* energies for the CO-CO interaction reported recently in a precise PIP-Neural Network (PIP-NN) form.[8] Dynamics calculations are done for the bare CO-NaCl, a cluster where a central CO is surrounding by four neighboring COs and a cluster with 12 surrounding COs. Isomerization is found in all cases; however, there are quantitative differences. The results for the largest cluster model are closest to the experiment. In cases isomerization is found to occur at distances from the NaCl that strongly point to a roaming mechanism, which is vibrationally ~~facilitate.~~ Calculated emission spectra corresponding to experiment,[5] are also given.

In the next section we present essential details of the new PES for the cluster, key properties and how they relate to the experiment. Quasiclassical trajectory calculations of the isomerization are reported and interpreted in terms of a large amplitude roaming-type mechanism that opens up upon high vibrational excitation of the CO stretch.

We note previous theoretical work on CO adsorbed on NaCl(100). These include a study of the structure of CO monolayer adsorbed on NaCl(100) from molecular dynamics[9] using model potentials, a perturbation theory study of an adlayer CO on NaCl(100) with consideration of CO-CO coupling,[10] a sophisticated kinetic model of CO-CO energy pooling,[11] a study of infrared fluorescence of a monolayer of ^{13}CO:NaCl(100) from highly vibrational excited states,[12] and a study of structures, energetics, and vibrational Davydov splittings.[13] None of these considered CO/OC isomerization. While the current paper was being revised, some of the current authors also reported PESs for CO interacting with NaCl(100) using density functional theory (DFT) and implications in isomerization of vibrationally excited CO.[14] The DFT PESs assume periodic boundary conditions, and thus are not suitable for dynamics calculations of CO isomerization.

Results

Potential Energy Surface

In order to model the isomerization dynamics of a monolayer of CO on NaCl(100) we make note of the following properties (and assumptions) of such a monolayer. (Note, that while it is reasonable to refer to Na as Na^{+} and Cl as Cl we do not do that below.) First, each CO is associated with a given Na on the surface and there is no migration of COs to other Na sites. However, since it is not possible to assign a single Cl to a given Na some consideration of the surrounding Cls must be given. Of the four nearest neighbor Cls only two are available for each CO in a monolayer and so each CO is shared by two Cls. This template for each CO and Na and two Cls is used to create a cluster model for the monolayer. There is a central CO molecule in this cluster that is surrounded by other CO molecules. Isomerization dynamics are modeled by vibrationally exciting the central CO. That CO interacts with other COs in a pairwise fashion and we consider the CO-CO interactions among the surrounding COs within a certain distance, which we describe below.

The PES corresponding to this model consists of a new *ab inito* PES for the CO-NaCl interaction with the Na-Cl distance fixed at 2.82 angstrom (the distance in NaCl(100)) plus an *ab inito* PES describing CO-CO interactions. Both PESs describe highly vibrationally excited CO. The CO-NaCl interaction PES is used in the Cl-sharing scenario by using an average of the CO-NaCl and CO-NaCl potentials where Cl and Cl denote the relevant shared Cls, as will be shown in detail below.

Details of CO-NaCl PES, which is a permutationally invariant polynomial (PIP) fit to 8592 energies and gradients at CCSD/aug-cc-pVDZ level of theory and which describes the C-down and O-down minima, are given in the Supplementary Information (SI). The PIP PES describing the CO-CO interaction is also described in the SI. This PES is a refit the PIP-NN PES.[8] The PIP re-fit is done to have fast evaluation of energy and analytical gradients. A final aspect of this model is the treatment of the interaction of CO with Cl. For isolated CO-NaCl the CO and NaCl are coplanar with the O end pointed towards the Cl (as expected) as discussed in detail in the SI. For the O-down isomer all atoms are also coplanar with C end pointed to the Cl. This is not qualitatively correct for a monolayer of CO on the NaCl surface where the CO axis is not coplanar with Na and Cl, as discussed in the recent DFT study.[14]

The approach to address this is to use the average potential for CO-NaCl and CO-NaCl where the Cl and Cl are nearest neighbors to a given Na. As shown in the SI the average CO-NaClCl potential gives a minimum with the CO axis bisecting the right triangle made by Na and two Cl. Geometry optimizations were performed using this average PES for both C-down and O-down isomers and the isomerization saddle-point. The energy of the O-down isomer is 766 cm ^{1} relative to the C-down isomer. Normal mode analyses were done at these stationary points and results are given in Table 7 of the SI. The imaginary frequency of the saddle point (SP) is 56*i* cm ^{1}, which indicates a flat isomerization barrier and likely roaming dynamics.

Depictions of the two minima of this average potential are shown in Fig. 1. As seen, the CO-axis of the C-down and O-down minima lie along a 45 deg bisector of the X-Y plane defined by NaCl and NaCl . The C-down minimum has a polar (tilt) angle of 34 degrees with respect to the normal to the plane of this triangle (the Z-axis in the figure). The O-down minimum has a tilt angle of 51 deg. These agree well with the experimentally reported tilt angles of about 25 and 45 deg, respectively.[5]

We now turn to the cluster model consisting of a central CO with 12 surrounding COs and 18 NaCls. This cluster is depicted in Fig. 2 for the C-down and O-down minima. At the former all COs are C-down and oriented in the same way; for the O-down minimum we indicate this isomer only for the central CO. The total potential is expressed as sum of all 13 CO-NaClCl average potentials and CO-CO 2-body interactions. Note, it is not necessary to consider all (78) CO-CO interactions, because most are weak owing to the large distances between many pairs. At equilibrium, the nearest-neighbor CO-CO distance between centers of mass is 3.99 angstrom. Next nearest neighbors are 5.64 angstrom apart. Restricting to these, there are 32 CO-CO interactions and these range from -123 to -15 cm ^{1}.

Because the CO-CO interactions are weak compared to the interaction between the COs and the associated NaClCl units the CO equilibrium configurations are expected to be close to those for the averaged CO-NaClCl potential. Thus, full geometry optimzation of this 62-atom cluster was not done. Geometry optimization and normal mode analyses were performed for the central CO using this cluster PES for both C-down and O-down isomers. The energy of the O-down isomer is 729 cm ^{1} relative to the C-down isomer. This is close to the 766 cm ^{1} energy difference for the average CO-NaClCl potential. (This energy difference is similar to the energy difference of around 750 cm ^{1} based on an electrostatic model without short-range interactions and at a fixed distance of the CO above the surface.[6])

Normal mode frequencies of the central CO at the stationary points are given in Table 8 in the SI. The CO-stretch has frequencies of 2171 and 2080 cm ^{1} for the C-down and O-down isomers, respectively. These are respectively blue (+44 cm ^{1}) and red-shifted (-47 cm ^{1}) relative to the harmonic frequency of the isolated CO (from the PES). These are in qualitative agreement with experiment; however, the values of the shifts are larger than seen in the experiment. The normal mode frequencies of the frustrated CO rotations and translations are in the range 10 to 220 cm ^{1} for the minima.

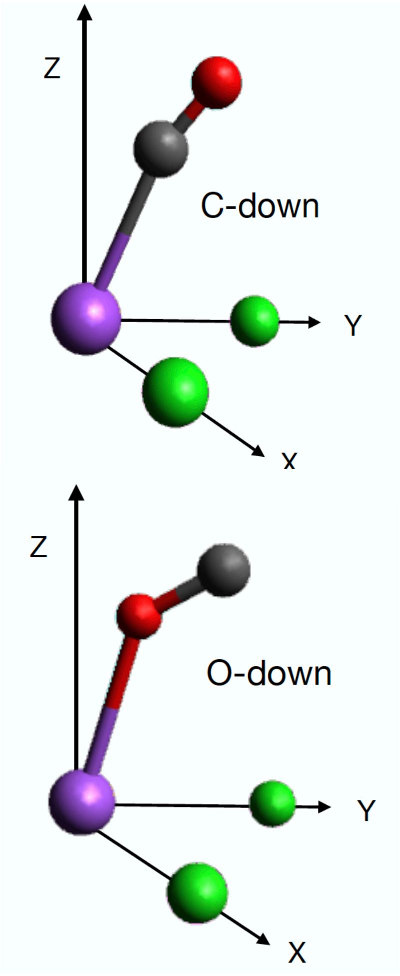

Figure 1. Structures of the C-down and O-down minima from the average CO-NaCl potential, described in the text. C is indicated by dark gray, O by red, Na by purple and Cl by green.

In anticipation of the dynamics calculations, which focus on vibrationally excited CO, we show several plots that indicate the change in energetics for highly stretched CO. The first are one-dimensional plots of unrelaxed potentials as a function of for two values of r_{CO}. These potential cuts are shown in Fig. 3. In these plots the CO is simply rotated about an axis perpendicular to the plane of the figure showing the C-down equilibrium configuration in Fig. 1. The angle is defined precisely in the SI and all other coordinates are fixed at the C-down minimum. For CO at equilibrium the (unrelaxed) isomeriation barrier is roughly 2700 cm ^{1} but in the stretched case it is roughly half that value, relative to the C-down minimum. Note the large change in the O-down minimum relative to the C-down one. Next are contour plots of the interaction potential of the central CO, shown in Fig. 4. In these the Z-component of the position vector of the center of mass of the central CO is the additional variable. In the the upper plot with r_{CO} at r_e the deeper minimum at 146 deg is C-down and the unrelaxed barrier is at around 230 deg and at Z of about 5 angstrom. For r_{CO} equals 1.59 angstrom the unrelaxed O-down minimum is much deeper than the C-down minimum and also spans a much large space than the C-down minimum and the unrelaxed barrier moves to nearly 6 angstrom. Another difference is the extent of anisotropy in for the stretched-CO plot. As seen this region extends to Z-values greater than 8.0 angstrom. These changes are relevant the dynamics presented next (and also to experiment where isomerization is seen when the CO

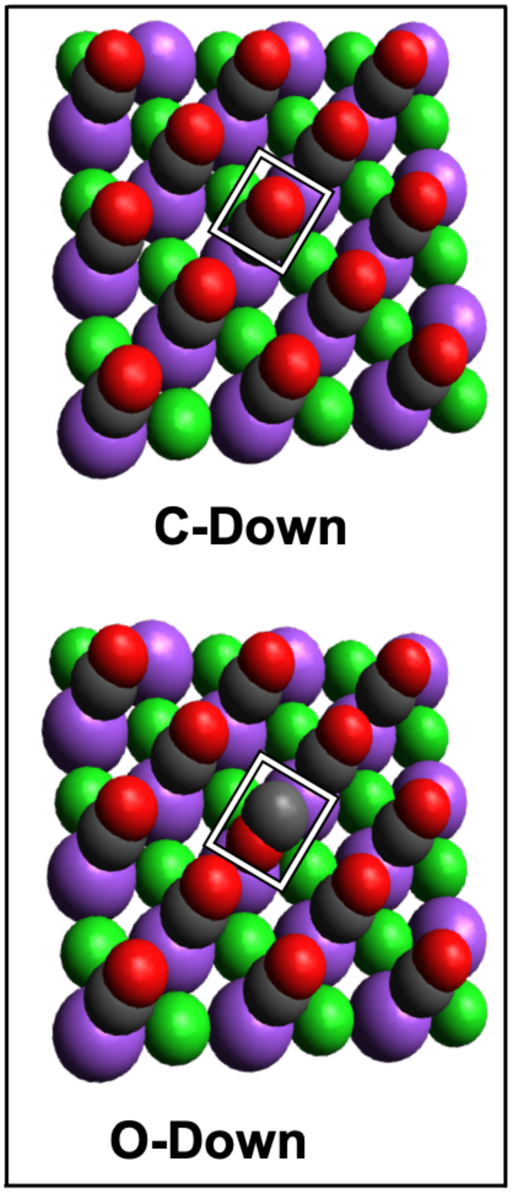

Figure 2. Depictions of the central CO C-down and O-down isomers for the cluster with 13 COs. C is indicated by dark gray, O by red, Na by purple and Cl by green.

(C-down) is highly vibrationally excited[5]).

From these plots we expect different dynamics for CO in the ground and this highly excited vibrational state. For the latter where the interaction extends to large distances above the surface, roaming[15–17] is likely. This is confirmed from analysis of the dynamics calculations given next.

Quasiclassical Trajectory Calculations

The initial conditions for the large cluster have the central C-down CO vibrational excited. This is done by stretching the CO to an outer turning point and keeping all the 12 COs at their equilibrium value. An additional amount of kinetic energy of 300 cm^{-1} is added randomly and microcanonically to other degrees of freedom of the central CO to account for the thermal energy corresponding to the experimental

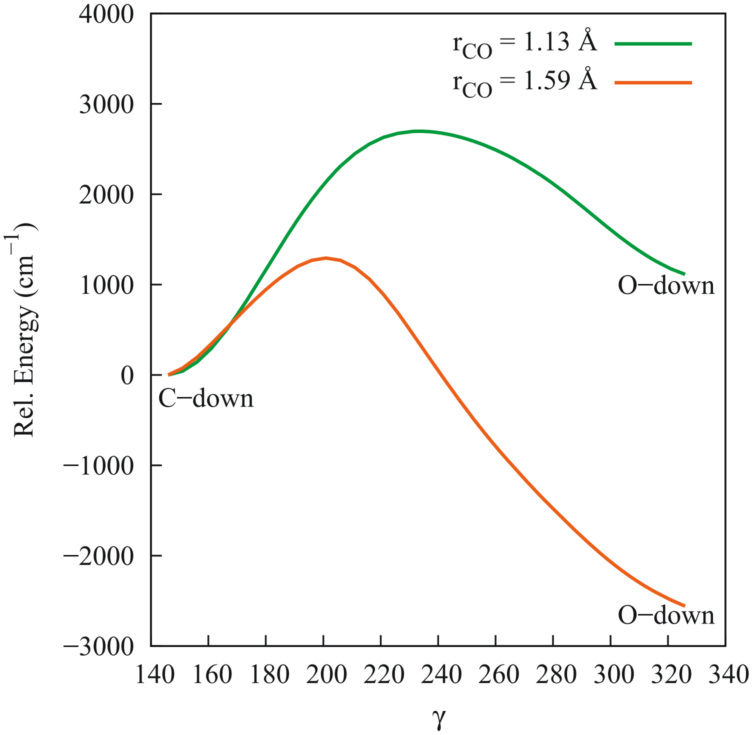

Figure 3. 1-D, unrelaxed potential cuts as a function of γ (deg) relative to the C-down isomer for the indicated values of r_{CO} corresponding to $v = 0$ (1.13 angstrom) and the outer turning point for $v = 20$ (1.59 angstrom) vibrational states.

temperature of 7 K.[5] The NaCl bond distance is fixed at 2.82 angstrom during the propagation of each trajectory. 500 trajectories were run for each vibrational state v and each trajectory was run for a maximum of 200,000 time steps (roughly 20 ps). Details are given in the SI. As a trajectory propagates we monitor the Na-C and Na-O distances. If they become nearly equal we examine the trajectory in detail to determine if and for how long the Na-O distance is shorter than the Na-C one. This is our criterion for isomerization.

Such trajectory calculations were also done for the bare CO-NaCl and the smaller cluster with 4 surrounding COs. In all cases, we observed isomerization based on the above criterion, desorption, or failure of the trajectory (after 200 000 time steps) due to unphysical edge effects of the finite cluster where some of the outermost COs sample configurations that are far from those described by the average CO-NaClCl′ PES.

For the bare NaCl-CO, we observed isomerization starting at v = 12. For v = 15 and above desorption is the major outcome. While this is not unexpected (since the total energy of the CO is more than ten times the dissociation energy), it is at odds with experiment, which has little or no desorption. For the small, 5 CO-cluster isomerization starts at v = 16 and desorption does not become a major process until v = 20. For the large 13-CO cluster we performed ~~QCT~~ calculations for v = 16,18,20,22 and 24. In this case isomerization starts when v = 22 which is in much closer accord with experiment. So adding the CO-CO interactions suppresses desorption and also moves isomerization to higher vibrational states. We discuss this further below.

For the large cluster for v = 22, 63 trajectories isomerized, only 9 trajectories directly desorbed, 32 trajectories completely propagated for 200 000 time steps without any isomerization or desorption. The remaining 396 eventually failed due to the edge effect mentioned above. For v = 24 we observed 126

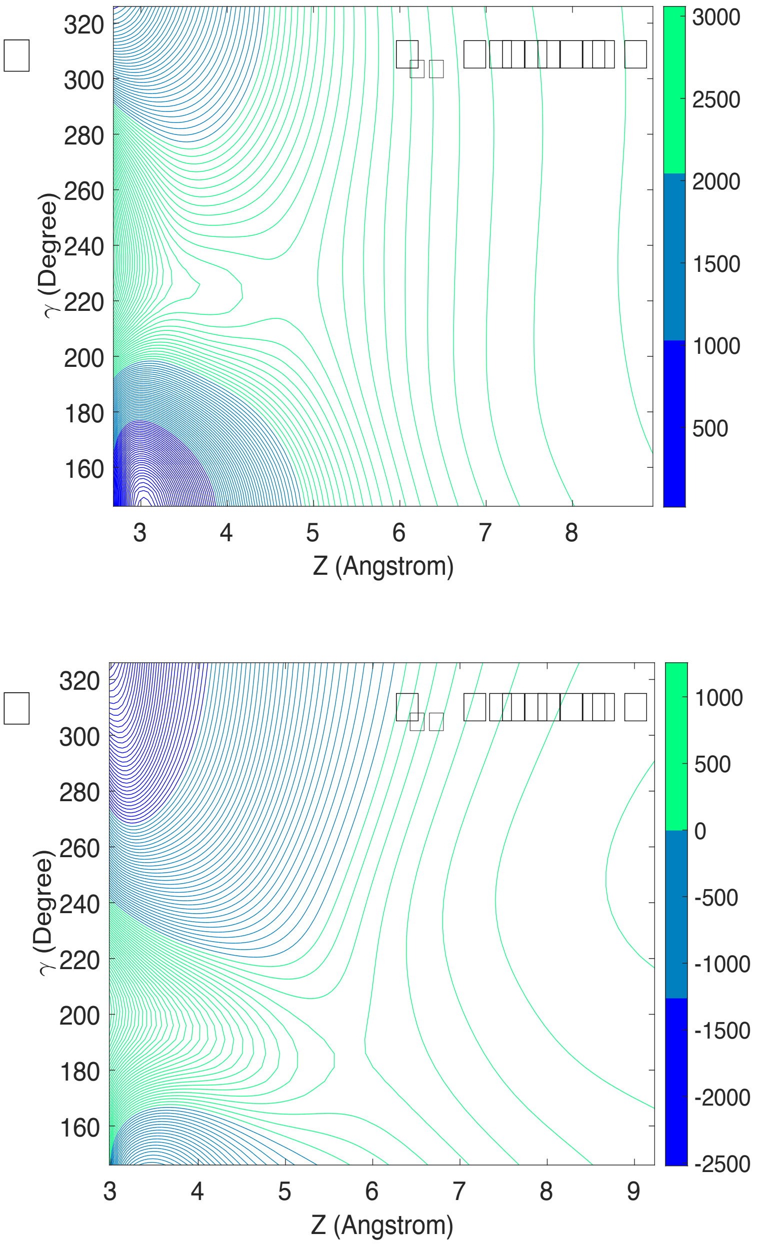

Figure 4. Contour plots for the large cluster PES in the variables Z and , defined in the text, for the indicated values of r_{CO}. Contour values are in 31 cm ^{1} increments for the top one and 38 cm ^{1} increments for the below one.

isomerizing trajectories, 185 desorbed and only 2 trajectories completely propagated for 200 000 times steps. The remainder failed due to the edge effect. In total, there were 189 isomerizing trajectories for these two vibrational states. For these, we calculated the value of Z where the Na-C and Na-O distances are first about equal. A histogram of these Z-values is shown in Fig. 5. As seen, the major peak is at around 5-6 angstrom; this is much larger than the conventional SP distance of 3.0 angstrom.

Plots of the time dependence of Z and the interaction potential of an isomerizing trajectory for $v = 22$ are shown in Fig. 6. Initially the CO is at the C-down minimum with a stretched CO bond length and Z is at the equilibrium value. Z increases with time and reaches a plateau value of around 4.7 angstrom before

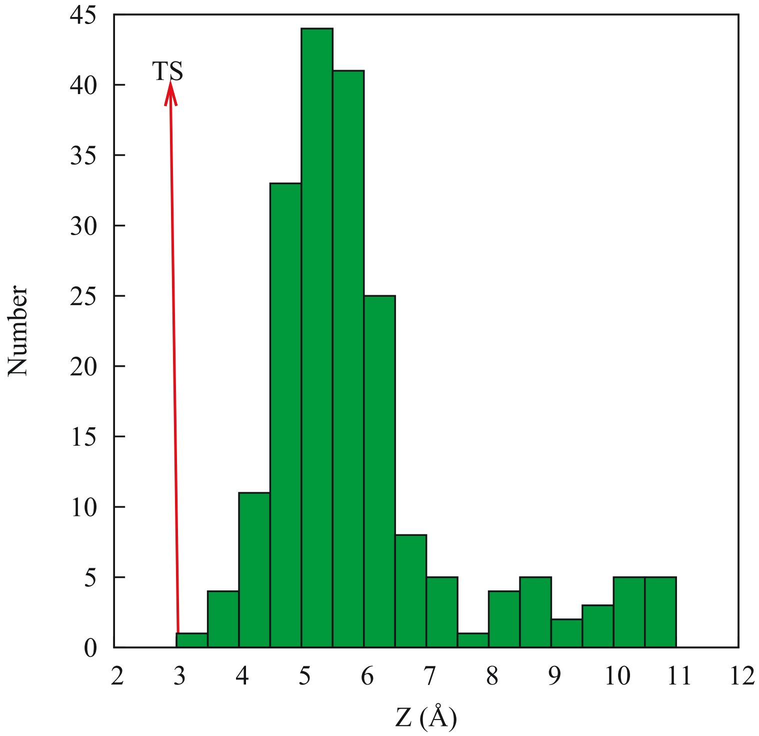

Figure 5. Histogram of the distribution of Z, the distance above the surface, for isomerizing trajectories for $v = 22$ and 24. The red arrow indicates the value of Z at the saddle point transition state for the average CO-NaCl potential.

declining again to less than 2.5 angstrom. The corresponding interaction potential oscillates strongly except in the plateau region. This behavior can be understood as follows. At early times the C-down CO stretch is interacting with NaCl surface largely based on ion-dipole forces. At times after isomerization the O-down CO-stretch is similarly interacting (albeit more strongly) with the surface. In both cases the dipole moment of the highly excited CO changes sign as the molecule compresses and stretches (see Fig. 13 in SI for a plot of the dipole moment vs r_{CO}.) Thus, if the total interaction is mostly due to dipole-ion interactions, the oscillation in the dipole moment explains the oscillations of the interaction potential. By contrast, at large Z the potential is nearly flat. This is because of longer range and hence a smaller interaction and also because the CO dipole is nearly parallel to the surface as so the dipole interaction is much reduced.

This plateau region both in Z and the potential at long range where isomerization occurs satisfies the general conditions of roaming.[15, 18] A plot of the C and O distances to the Na atom is shown in Fig. 8 in the SI for this trajectory. This plot shows the early history of the trajectory where C is closer to Na than O, the plateau region where the two distances are nearly equal (and also the point where they are equal) and the later part of the trajectory where the O atom is closer to the Na.

Snapshots of a representative isomerizing trajectory for $v = 22$ are shown in Fig. 10 in the SI. These are taken from an animation that is also available as a separate file. As seen the CO initially separates from the NaCl and isomerization begins at where thus, isomerization predominatly occurs at values of R much larger than the SP value.

Another important result of the present calculations is that CO is vibrationally excited after isomerization. This is indicated in Fig. 9 in the SI which shows r_{CO} as a function of time prior to and then after

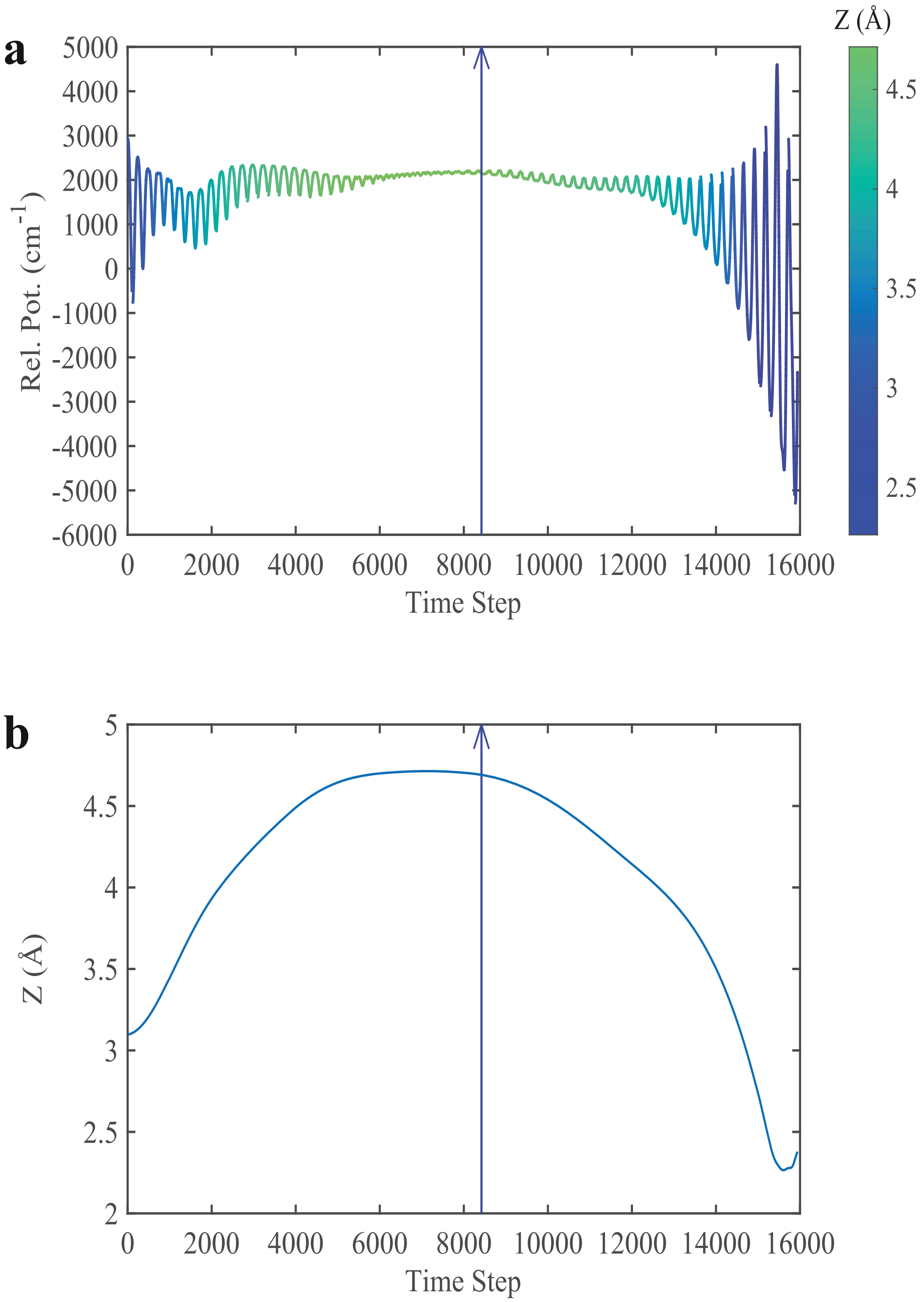

Figure 6. Time dependence of the interaction potential (a) and Z, the distance above the surface (b) for an isomerizing trajectory for v=22 for the large cluster. The vertical arrow indicates the time at which the isomerization occurs.

isomerization, for CO $v = 22$. As seen, the O-down isomer remains in this state and so emission from this state for the O-down isomer can occur.

We calculated the emission spectra for Δ-v = -2 transitions of the C-down and O-down isomers. Details of this calculation are given in the SI. As shown, the two spectra are interleaved with both showing increasing intensity and decreasing overtone gaps as v increases, in agreement with experiment.

Discussion

The present ~~trajectory~~ calculations find that isomerization occurs only for highly excited vibrational states of the C-down isomer. The threshold for isomerization increases as surrounding COs are added to the bare CO-NaCl moiety, with the threshold at $v = 22$ for the 13-CO cluster mode. This threshold is consistent with the experiment, which shows emission from the C and O-down isomers for vibrational states up to v of 27. Second, the present calculations show that CO continues to be highly vibrationally excited after isomerization. This is also clearly in agreement with experiment. Also, from the calculations, it appears that emission from much lower-lying O-down vibrational states seen in experiment occurs not from prompt isomerization but from relaxation of higher vibrationally excited O-down CO.

The driving force for this vibrationally induced isomerization is the major change in the potential energy surface from energetically favoring the C-down isomer to greatly favoring the O-down isomer upon high vibrational excitation of the CO-stretch. Also, the region of interaction between the CO and NaCl extends to longer range upon high vibrational excitation. The isomerization dynamics thus occurs over large range of distances of the CO from the NaCl surface, very reminiscent of roaming.[15–17] For the specific case of isomerization, recall that roaming was reported in unimolecular dissociation of energized CH_3NO_2.[18–21] In this case internally excited CH_3NO_2 can undergo a frustrated dissociation to fragments, CH_3 and NO_2, where the incipient fragments roam at large distance in a flat part of the potential and go on to form CH_3O+NO products.

Finally, we make some comments of the effects of CO-CO interactions on the central active CO. These interactions provide a channel for energy transfer from the vibrationally excited CO. This qualitatively at least accounts for the increase in the threshold for isomerization in going from NaCl-CO to the small 5-CO cluster to the larger 13-CO cluster. Second, the large amount of desorption observed for bare NaCl-CO is reduced for the small CO-cluster and further reduced for the 13-CO cluster. Some of this effect can again be accounted for by the CO-CO energy transfer. Also, because the CO-CO interactions are attractive, the effect of them is to increase the dissociation energy (which we estimate to be roughly 600 cm ^{1}), which also results in less desorption. More details about dissociation energies are given in the SI.

The calculated IR overtone emission spectra are in accord with the experimental ones in showing significant intensity for high v-states.[5] The present calculations find a threshold for isomerization at $v = 22$, whereas experiment cannot determine such a threshold from the emission spectra. There are indeed strong experimental emission lines for the O-down isomer in the region of v = 20-28, but also a long progression at lower v all the way down to around $v = 4$. The present calculations interpret these lines below around 20 as due to vibrational relaxation of the highly excited O-down isomer and not prompt emission following isomerization of the C-down isomer in these low v states.

In summary, the present calculations verifies the vibrationally induced isomerization reported experimentally dominated by a roaming pathway, where the isomerization occurs at large separations, roughly 5 angstroms larger than the separation at the conventional isomerization saddle point. There are aspects of the experiment that will need to be addressed in future work. One is the details of the energy pooling that is needed to prepare CO in highly excited vibrational states. Another is the relaxation of highly excited O-down isomers and the subsequent reformation of the C-down isomer.

Methods

Details of all the calculations reported here are given in the Supplementary Information.

Data Availabilty

All data shown here and in the Supporting Information are available in files provided.

Code Availabilty

The potentials reported in the paper are available in compressed folders as supporting information.

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References

1. Bowman, J. M., Gazdy, B., Bentley, J. A., Lee, T. J. & Dateo, C. E. Ab initio calculation of a global potential, vibrational energies, and wave functions for HCN/HNC, and a simulation of the $\tilde{A}$-$\tilde{X}$ emission spectrum. *J. Chem. Phys.* **99**, 308–323 (1993).
2. Bowman, J. M. Beyond platonic molecules. *Science* **290**, 724–725 (2000).
3. Zou, S., Bowman, J. M. & Brown, A. Full-dimensionality quantum calculations of acetylene vinylidene isomerization. *J. Chem. Phys.* **118**, 10012–10023 (2003).
4. DeVine, J. A. *et al.* Encoding of vinylidene isomerization in its anion photoelectron spectrum. *Science* **358**, 336–339 (2017).
5. Lau, J. A. *et al.* Observation of an isomerizing double-well quantum system in the condensed phase. *Science* **367**, 175–178 (2020).
6. Chen, L. *et al.* The sommerfeld ground-wave limit for a molecule adsorbed at a surface. *Science* **363**, 158–161 (2019).
7. Vogt, J. & Vogt, B. The structure of carbon monoxide adsorbed on the NaCl(100) surface: A combined LEED and DFT-D/vdW-DF study. *J. Chem. Phys.* **141**, 214708 (2014).
8. Chen, J., Li, J., Bowman, J. M. & Guo, H. Energy transfer between vibrationally excited carbon monoxide based on a highly accurate six-dimensional potential energy surface. *J. Chem. Phys.* **153**, 054310 (2020).
9. Hoang, P. N. M., Picaud, S., Girardet, C. & Meredith, A. W. Structure of CO monolayer adsorbed on NaCl(100) from molecular dynamics. *J. Chem. Phys.* **105**, 8453–8462 (1996).
10. Meredith, A. W. & Stone, A. J. A perturbation theory study of adlayer CO on NaCl(100). *J. Chem. Phys.* **104**, 3058–3070 (1996).
11. Corcelli, S. A. & Tully, J. C. Vibrational energy pooling in CO on NaCl(100): Methods. *J. Chem. Phys.* **116**, 8079–8092 (2002).
12. Boney, E. T. D. & Marcus, R. A. On the infrared fluorescence of monolayer ^{13}CO:NaCl(100). *J. Chem. Phys.* **139**, 184712 (2013).
13. Boese, A. D. & Saalfrank, P. CO molecules on a NaCl(100) surface: Structures, energetics, and vibrational Davydov splittings at various coverages. *J. Phys. Chem. C* **120**, 12637–12653 (2016).
14. Chen, J., Hariharan, S., Meyer, J. & Guo, H. Potential energy landscape of co adsorbates on NaCl(100) and implications in isomerization of vibrationally excited CO. *J. Phys. Chem. C* **124**, 19146–19156 (2020).
15. Townsend, D. *et al.* The roaming atom: Straying from the reaction path in formaldehyde decomposition. *Science* **306**, 1158–1161 (2004).
16. Suits, A. G. Roaming atoms and radicals: A new mechanism in molecular dissociation. *Accounts Chem. Res.* **41**, 873–881 (2008).

17. Bowman, J. M. & Shepler, B. C. Roaming radicals. *Annu. Rev. Phys. Chem.* **62**, 531–553 (2011).

18. Homayoon, Z. & Bowman, J. M. Quasiclassical trajectory study of CH_3NO_2 decomposition via roaming mediated isomerization using a global potential energy surface. *J. Phys. Chem. A* **117**, 11665–11672 (2013).

19. Zhu, R. & Lin, M. CH_3NO_2 decomposition/isomerization mechanism and product branching ratios: An ab initio chemical kinetic study. *Chem. Phys. Lett.* **478**, 11 – 16 (2009).

20. Dey, A. *et al.* Photodissociation dynamics of nitromethane and methyl nitrite by infrared multiphoton dissociation imaging with quasiclassical trajectory calculations: Signatures of the roaming pathway. *J. Chem. Phys.* **140**, 054305 (2014).

21. Wodtke, A. M., Hintsa, E. J. & Lee, Y. T. Infrared multiphoton dissociation of three nitroalkanes. *J. Phys. Chem.* **90**, 3549–3558 (1986).