Vibrational Excitation Hindering an Ion-Molecule Reaction: The c-$C_3H_2^+$ – H_2 Collision Complex

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Experiments within a cryogenic 22-pole ion trap have revealed an interesting reaction dynamic phenomenon, where rovibrational excitation of an ionic molecule slows down a reaction with a neutral partner. This is demonstrated for the low-temperature hydrogen abstraction reaction c-$C_3H_2^+ + H_2$, where excitation of the ion into the ν_7 antisymmetric C-H stretching mode decreased the reaction rate coefficient toward the products c-$C_3H_3^+ + H$. Supported by high-level quantum-chemical calculations, this observation is explained by the reaction proceeding through a c-$C_3H_2^+ - H_2$ collision complex in the entrance channel, in which the hydrogen molecule is loosely bound to the hydrogen atom of the c-$C_3H_2^+$ ion. This discovery enables high-resolution vibrational action spectroscopy for c-$C_3H_2^+$ and other molecular ions with similar reaction pathways. Moreover, a detailed kinetic model relating the extent of the observed product depletion signal to the rate coefficients of inelastic collisions reveals that rotational relaxation of the vibrationally excited ions is significantly faster than the rovibrational relaxation, allowing for a large fraction of the ions to be vibrationally excited. This result provides fundamental insight into the mechanism for an important class of chemical reactions, and is capable of probing the inelastic collisional dynamics of molecular ions.

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Hydrogen abstraction reactions involving hydrocarbons play an important role in the formation of polycyclic aromatic hydrocarbons in combustion chemistry [1] and in the chemistry of the interstellar medium [2]. Even at low temperatures these reactions can be rapid, allowing for them to occur in the cold environments prevalent in the interstellar medium. This is especially true for reactions between charged and neutral molecules, e.g., the series of reactions $CH_n^+ + H_2 \rightarrow CH_{n+1}^+ + H$ ($n = 1, 2$) forming the smallest ionic hydrocarbons in space, where the reaction basically proceeds at the collision rate [3,4]. However, several of these reactions, like the one studied in this work:

$$\text{c-}C_3H_2^+ + H_2 \rightarrow \text{c-}C_3H_3^+ + H \tag{1}$$

are rather slow, and it can take thousands or even more collisions for the reaction to take place, despite the fact that it is exothermic [5,6].

The study of reaction dynamics seeks to understand the behavior of chemical reactions through the concept of a potential energy surface (PES), where the products and reactants are connected by a path through an energetic landscape. A central topic in reaction dynamics is the study of how molecular excitation (rotational, vibrational, electronic) influences the outcome of a chemical reaction. Simple atom-diatom reactions are found to follow Polanyi's rules—if the transition state resembles the reactants (early barrier) vibrational energy will have a small effect on the reactivity, and if the transition state resembles the products (late barrier) it will enhance the reactivity [7]. These guidelines have stood the test of time; however, it is challenging to extend them to larger systems like reaction (1) which do not have an obvious reaction path on the multidimensional PES and have additional vibrational degrees of freedom.

A series of pioneering experiments on the reaction between HOD and H to form OH or OD were the first to demonstrate vibrational selectivity of the product channel [8–13], where even a single vibrational quantum in the OH stretching mode could greatly promote cleavage of the OH bond. The effect that the PES has on vibrational control was systematically investigated by crossed-beam studies on hydrogen abstraction from CHD_3 [14]. These were tailored to mimic early and late barrier motifs of Polanyi's rules, and it was found that the late barrier reaction $CHD_3 + Cl \rightarrow CD_3 + HCl$ was enhanced by exciting the CH stretch [15]. Interestingly, it was also shown that for $CHD_3 + F \rightarrow CD_3 + HF$, an exothermic reaction with an early barrier transition state, excitation of the CH mode significantly decreased the rate by 80–90% [16], which could be rationalized using quasiclassical trajectory calculations [17,18].

It is often found in endothermic reactions that the addition of internal energy comparable to the energetic barrier will lead to a significantly larger reaction rate coefficient. This is consistent with Hammond's postulate, where endothermic reactions are expected to have a late barrier and therefore can be promoted by vibrational excitation [19], although one should be careful applying this to polyatomic systems. Such effects can be exploited for action spectroscopy of trapped and cooled ions, as realized in the method of laser induced reaction [20–24]. In addition to being a useful spectroscopic tool, these studies also provide a more detailed picture of the reaction dynamics. At very low temperatures, even the change in internal energy from rotational excitation substantially changes the total collision energy which in effect leads to rotational state-dependent attachment of rare gas atoms, and has been used to measure rotational transitions of molecular ions [25–27].

In this Letter, we probed reaction (1) at low temperature as an indicator of coupling between the reaction coordinate and vibrational excitation of c-$C_3H_2^+$. The rate coefficient of this reaction has previously been measured using a cryogenic 22-pole ion trap experiment, where it was observed to be quite small (5×10^{-13} cm^3 s^{-1} at 10 K) [6] (for a sample which probably contained a significant amount of the energetically higher lying l-$C_3H_2^+$). Based on a recent infrared (IR) overview spectrum of neon-tagged c-$C_3H_2^+$ [28], we chose the strong ν_7 antisymmetric C-H stretching fundamental at 3116 cm^{-1} as the vibrational excitation, which we naïvely expected to increase the reactivity. To our surprise, we discovered that vibrational excitation does not enhance the rate of reaction (1), but instead reduces it further. In this Letter, we report our experimental and theoretical investigations of this interesting dynamical phenomenon, which we have called laser induced hindering of a reaction (LIHR). Although there are other examples of vibrational inhibition [16,29], the measurements of reaction (1) provide unique insight into the prereaction complex of a prototypical carbocation hydrogen abstraction reaction, and they demonstrate a new method for probing fundamental inelastic collisional dynamics and photon processes.

The experiments have been carried out in the cryogenic 22-pole ion trapping instrument COLTRAP [30]. In brief, a pulse of several 10 000 $C_3H_2^+$ ions was generated in an ion source by electron impact of allene (C_3H_4), selected in a quadrupole mass spectrometer for mass 38 u, and then injected into the cryogenic 22-pole ion trap [31]. The trap was held at roughly $T = 9$ K and was constantly filled with hydrogen. During the trapping time of typically 400 ms, the cold c-$C_3H_2^+$ ion ensemble was continuously irradiated with narrow-bandwidth 3 μm IR radiation provided by a continuous wave optical parametric oscillator (Aculight Argos 2400) with power on the order of 100 mW. After the trapping period, the trap content was extracted, selected in a second quadrupole for a specific mass, and counted in a high-efficiency ion counter. The hydrogen density within the trap was estimated to be $\sim 5 \times 10^{11}$ cm^{-3} from the observed ratio of $C_3H_3^+$ to $C_3H_2^+$ after 400 ms trapping time and the known reaction rate coefficient at 10 K [6].

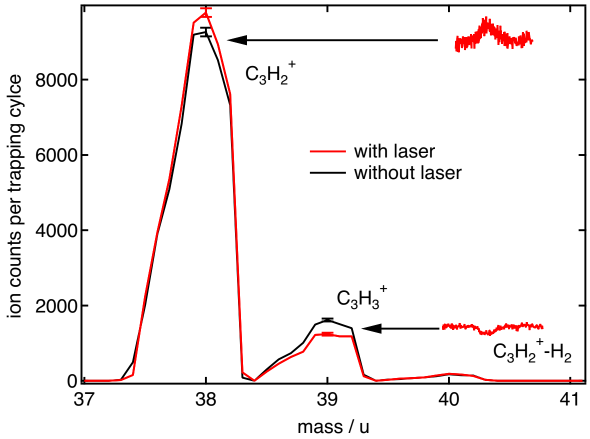

FIG. 1. Mass spectrum of the 22-pole trap content, in which injected $C_3H_2^+$ ions ($m = 38$ u) have been trapped for 400 ms in a 9 K hydrogen gas environment ($[H_2] \approx 5 \times 10^{11}$ cm^{-3}) and formed $C_3H_3^+$ ($m = 39$ u) through reaction (1). The red trace shows when the laser was resonant with a c-$C_3H_2^+$ rovibrational transition ($2_{02} \leftarrow 1_{01}$ at 3116.535 cm^{-1} of the ν_7 fundamental band in this case) and the black trace was recorded when the laser was off. The error bars at masses 38 and 39 represent the standard deviation of the ion counts. Insets show the c-$C_3H_2^+$ and c-$C_3H_3^+$ counts as a function of frequency, showing that the number of $m = 38$ u counts increases while the product $m = 39$ u counts decrease. c-$C_3H_2^+ - H_2$ complexes are seen as a small signal at $m = 40$ u.

The slowing down of reaction (1) upon vibrational excitation is demonstrated in the mass spectrum of Fig. 1. Here, the signal for the parent mass 38 u ($C_3H_2^+$) increases with resonant laser excitation while the product signal at 39 u ($C_3H_3^+$) decreases. The insets show the respective signals as a function of the excitation frequency of the IR laser, revealing clear spectral features of more $C_3H_2^+$ counts and less $C_3H_3^+$ counts at the same frequency position. This shows that the rovibrational excitation of c-$C_3H_2^+$ is further hindering this already slow reaction, which is a clear hint that the reaction mechanism must be more complex than originally expected. In addition, this demonstrates the sensitivity of the trap experiment, as a very slow reaction becomes even slower.

The c-$C_3H_2^+$ molecule is an asymmetric top of C_{2v} symmetry with an $\tilde{X}\ ^2A_1$ ground electronic state. Only a single rovibrational transition will be resonant with the laser at a given time, connecting a rotational level $N''_{K''_a K''_c}$ in the ground state to an excited $N'_{K'_aK'_c}$ in the $v_7 = 1$ state, where N is the rotational angular momentum, and K_a and K_c are related to its projection onto the molecular axes. A thorough spectroscopic analysis of all observed spectral features near 3116 cm^{-1} confirmed that they originated from c-$C_3H_2{}^+$, and more details on this are reported elsewhere [32]. The spectral feature in Fig. 1 was assigned to the $N_{K_aK_c} = 2_{02} \leftarrow 1_{01}$ rovibrational transition, and a detailed scan is shown in Fig. 2. The transition has unresolved fine structure due to c-$C_3H_2{}^+$ being open shell. Based on this assignment and the width of the narrowest lines, we estimate the kinetic temperature of the trapped c-$C_3H_2{}^+$ ions to be in the range of $T_{\mathrm{kin}} = 15$ K. The rotational temperature of the c-$C_3H_2{}^+$ ions was determined to be ~20.5 K [32]. Given the rotational temperature, the product count depletion of 10% in Fig. 2 is striking. The thermal population of the 1_{01} state is only 2.4% of the c-$C_3H_2{}^+$ ions, which is the only ground rotational state addressed in this transition.

For a direct reaction mechanism, where the colliding H_2 molecule might attack the bare carbon atom in the c-$C_3H_2{}^+$ ion, one might expect an increase in reactivity due to the additional internal energy from vibrational excitation. However, many low temperature ion-molecule and radical-molecule reactions are thought to proceed via an initial collision complex [34]. At low pressures, the activated complex will likely dissociate back to the reactants before it can be stabilized by another collision, with a small fraction overcoming the activation barrier to form the products [35]. There are hints that reaction (1) follows this scheme—in Fig. 1 there is a small but significant peak at mass 40 u, which corresponds to the mass of the c-$C_3H_2{}^+ - H_2$ complex adduct. As shown below, the geometry of the global minimum does not promote the reaction, and therefore its signal is found unchanged irrespective of whether c-$C_3H_2{}^+$ is excited or not.

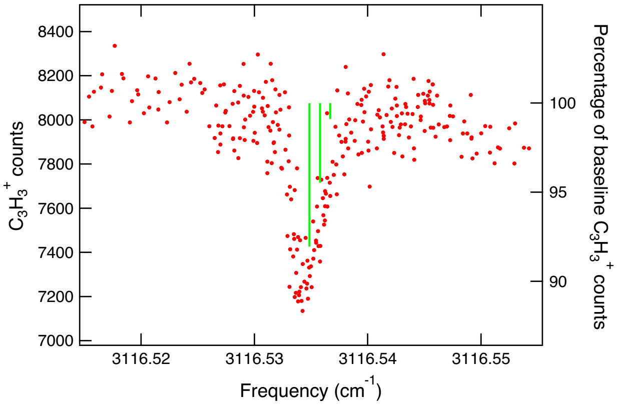

FIG. 2. A scan of the $2_{02} \leftarrow 1_{01}$ transition of the ν_7 fundamental band of c-$C_3H_2{}^+$. The rovibrational excitation hinders reaction (1) resulting in a reduction of $C_3H_3{}^+$ counts ($m = 39$ u). A simulation with PGOPHER [33] (green bars) reveals the transition to be composed of unresolved fine structure components.

High-level quantum chemical calculations were performed in order to understand the nature of the intermediate complex and the stable c-$C_3H_2{}^+ - H_2$ complex adduct. A preliminary set of calculations was performed at the coupled-cluster level of theory with single and double excitations, augmented with a perturbative treatment of triple excitations, CCSD(T) [36], using the correlation consistent cc-pVTZ basis set [37] and the frozen core (fc) approximation. All calculations have been performed using either the CFOUR suite of programs [38] or the GAUSSIAN16 [39] suite of programs interfaced with CFOUR. Further details can be found in the supporting information [40].

A scan of the c-$C_3H_2{}^+ - H_2$ potential energy surface was performed in order to locate stable complexes. Two complexes were located and their structures confirmed to be minima through a calculation of harmonic frequencies. Their structures were further refined at the CCSD(T) level of theory, correlating all electrons and employing the aug-cc-pCVQZ basis set [43,44], in order to have a quantitative assessment of the reaction energetics. The global minimum (energy with respect to the reactants -7.0 kJ mol^{-1}) corresponds to the complex where the H_2 molecule lies in the c-$C_3H_2{}^+$ molecular plane (Fig. 3, structure 1). The other local minimum, which is 1.4 kJ mol^{-1} higher in energy than the global minimum, is the complex where the H_2 molecules lies on the symmetry plane orthogonal to the $C_3H_2{}^+$ molecular plane (Fig. 3, structure 3).

A transition state connecting the two aforementioned minima was found. Unfortunately, it was not possible to optimize its structure at the higher level of theory due to hardware limitations. Nevertheless, calculations performed at the CCSD(T)/cc-pVTZ (fc) level, which for all the other species produced consistent results with respect to the

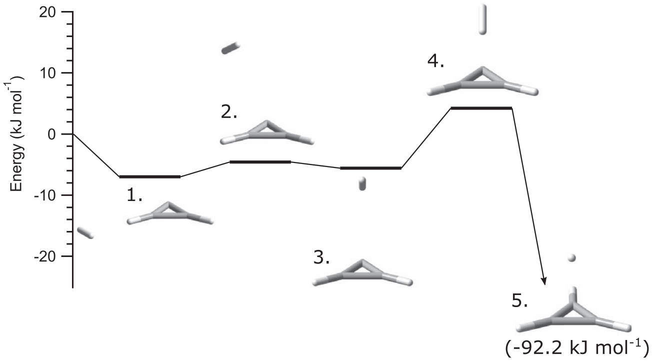

FIG. 3. Structures and energies relative to the reactants: From left to right, the global minimum (1: -7.0 kJ mol^{-1}), internal transition state (2: -4.7 kJ mol^{-1}), reactive local minimum (3: -5.6 kJ mol^{-1}), reactive transition state (4: $+4.2$ kJ mol^{-1}) and products (5: -92.2 kJ mol^{-1}). All structures and relative energies were computed at the CCSD(T)/aug-cc-pCVQZ level, except for the internal transition state, 2, which was calculated at the fc-CCSD(T)/cc-pVTZ level.

higher level ones, produced a barrier height of 2.3 kJ/mol. Therefore, we can conclude that the isomerization between the two minima is not a limiting step for the reaction. A reactive transition state (Fig. 3, structure 4) was located starting from the structure of the local minimum. Following the reaction coordinate, the local minimum is on one side of the transition state, with the products on the other (Fig. 3, structure 5). The reactive transition state and reaction energy were also calculated at the CCSD(T)/aug-cc-pCVQZ level, and were located at $+4.2\ \mathrm{kJ\,mol^{-1}}$ (505 K) and $-92.2\ \mathrm{kJ\,mol^{-1}}$.

The combined experimental and theoretical investigation provides a clear picture of how the reaction (1) proceeds—at 15 K the ions have insufficient thermal energy to overcome the $4.2\ \mathrm{kJ\,mol^{-1}}$ barrier but are able to form a collision complex which is followed by tunneling through the reaction barrier. In fact, the reaction has to proceed during the short lifetime of the activated complex, and therefore this reaction is competing with stabilization or dissociation of the complex, which is unavoidable as the total energy of the complex is above the dissociation limit back towards the reactants. Upon vibrational excitation of the c-$C_3H_2^+$ reactant, complex formation is inhibited and a net reduction of the reaction rate is detected. However, an explanation is still needed for the size of the depletion signal, which exceeds the thermal population of the initial state.

To qualitatively understand the strength of the LIHR signals, a model of the collision and photon related processes within the trap was constructed. A schematic is shown in Fig. 4. Only ions in the initial ($N''_{K''_aK''_c}$) and final ($N'_{K'_aK'_c}$) rotational states can interact with the light, and are labeled N_I and N_{II}, while the remaining populations in the ground and $v_7 = 1$ states are labeled n_I and n_{II}. Ions in population N_I will absorb the mid-IR light at a rate of $\rho B_{12} N_I$, where ρ is the spectral energy density of the light source and B_{12} is the Einstein B coefficient for absorption. Vibrationally excited ions can return to the ground state either through stimulated emission from state N_{II} at a rate $\rho B_{21} N_{II}$, and all ions in the $v_7 = 1$ state can return through spontaneous emission or vibrational relaxation from collisions at rates $A_{21} N_{II}$, and $k_{\mathrm{vib}}[H_2]N_{II}$ respectively, where A_{21} and B_{21} are the Einstein A and B coefficients for spontaneous and stimulated emission, respectively, and k_{vib} is the collisional vibrational relaxation rate coefficient.

Collisional relaxation of the rotational states towards their thermal populations is assumed to be highly efficient, occurring nearly at the collisional rate, k_{col} [45–49]. As a simple model of this process, each collision with H_2 is considered to have a chance of transferring ions between N_i and n_i with a probability determined by the thermal population fraction of N_i.

A calculation of the time-dependent populations at three different hydrogen densities was performed considering the transition in Fig. 2 ($2_{02} \leftarrow 1_{01}$). The Einstein coefficients were determined using the recently reported ν_7 band strength of $137\ \mathrm{km\,mol^{-1}}$ [28]. The Langevin rate was used for the collisional rate ($1.5 \times 10^{-9}\ \mathrm{cm^3\,s^{-1}}$), and vibrational relaxation was assumed to occur from one out of every hundred collisions in agreement with earlier findings for ion-molecule collisions [20,50–53].

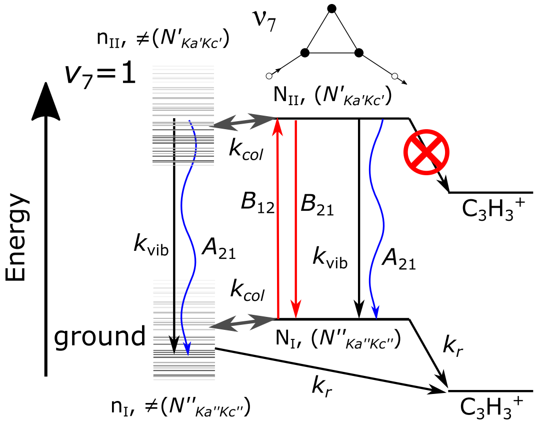

FIG. 4. A schematic of the processes involved in LIHR for a transition $N'_{K'_aK'_c} \leftarrow N''_{K''_aK''_c}$ with upper and lower populations N_{II} and N_I. A_{21}, B_{12}, and B_{21}: Einstein coefficients, n_I and n_{II}: populations which cannot interact with the mid-IR light in the ground and $v_7 = 1$ states, respectively, which are represented by the horizontal lines, k_{vib}: vibrational relaxation, k_{col}: inelastic collisions, k_r: rate coefficient for reaction (1).

The results are shown in Fig. 5, which reveals a clear mechanism for the large suppression in reactivity. The $v_7 = 1$ state rapidly becomes populated (<20 ms) as inelastic collisions transfer ions to rotational states other than $N'_{K'_aK'_c}$ where they are shielded from stimulated emission and cannot react, and collisions repopulate the initial $N''_{K''_aK''_c}$ state. This allows for more ions to become excited than are in the thermally populated $N''_{K''_aK''_c}$ state. Given the slow rate of collisional vibrational relaxation under the experimental conditions, spontaneous emission dominates with an Einstein A coefficient for the band of $167\ \mathrm{s^{-1}}$. Increasing the hydrogen density increases the rate of inelastic collisions, further increasing the fraction of unreactive ions. After 400 ms, laser excitation reduces the number of c-$C_3H_3^+$ ions formed by 6.5%, 10%, and 14% for $[H_2] = 5 \times 10^{11}$, 1×10^{12}, and $2 \times 10^{12}\ \mathrm{cm^{-3}}$, respectively. Although the calculation using our experimental number density of $5 \times 10^{11}\ \mathrm{cm^{-3}}$ shows only a 6.5% reduction versus the observed value of 10%, given the uncertainties associated with $[H_2]$ and k_r it is in strong qualitative agreement. More details regarding the model are given in the Supplemental Material [40].

In summary, the hydrogen abstraction reaction between c-$C_3H_2^+$ and H_2 to form c-$C_3H_3^+$ and H is a slow reaction at low temperatures and practically inhibited upon vibrational excitation. Detailed quantum chemical calculations show that the reaction proceeds via a collision complex in the entrance channel. The formation of such a complex is

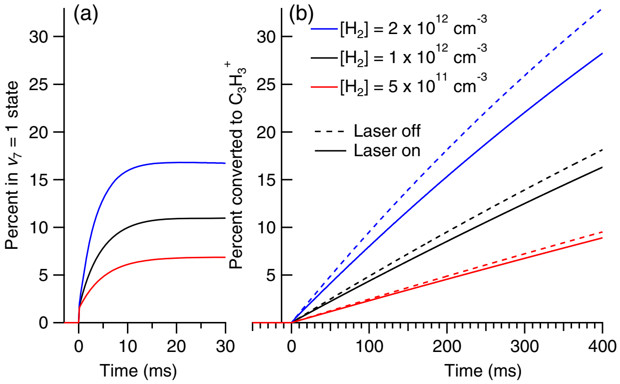

FIG. 5. The results of the kinetics model at three different H_2 densities. (a) The percentage of all ions within the trap in the vibrationally excited $v_7 = 1$. (b) The percentage of c-$C_3H_2{}^+$ ions converted to c-$C_3H_3{}^+$ with the laser on (solid lines) and laser off (dashed lines). Time 0 marks the time the ions are exposed to the laser light and the H_2.

inhibited upon the vibrational excitation which leads to the observed $C_3H_3{}^+$ product depletion signal. A model describing the kinetics of collisional processes as well as photon related processes reveals that rotational relaxation of vibrationally excited parent molecules is significantly faster than vibrationally inelastic collisions and radiative relaxation. In future studies these findings can be used to determine detailed rate coefficients from density dependent (i.e., collision dependent) measurements of depletion signals. Such rate coefficients for inelastic collisions are desirable for modeling thermal ensembles such as plasmas in the interstellar medium but are difficult to determine by other means. This phenomenon can also be used as a tool for action spectroscopy for many ions other than c-$C_3H_2{}^+$ studied here that are thought to occur through a similar mechanism.

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[1] H. Wang, Formation of nascent soot and other condensed-phase materials in flames, Proc. Combust. Inst. **33**, 41 (2011).

[2] R. I. Kaiser, D. S. N. Parker, and A. M. Mebel, Reaction dynamics in astrochemistry: Low-temperature pathways to polycyclic aromatic hydrocarbons in the interstellar medium, Annu. Rev. Phys. Chem. **66**, 43 (2015).

[3] D. Smith and N. Adams, Some positive ion reactions with H_2: Interstellar implications, Mon. Not. R. Astron. Soc. **197**, 377 (1981).

[4] D. Smith and N. Adams, Reaction of simple hydrocarbon ions with molecules at thermal energies, Int. J. Mass Spectrom. **23**, 123 (1977).

[5] M. W. Wong and L. Radom, Thermochemistry and ion-molecule reactions of isomeric $C_3H_2{}^+$ cations, J. Am. Chem. Soc. **115**, 1507 (1993).

[6] I. Savić and D. Gerlich, Temperature variable ion trap studies of $C_3H_n^+$ with H_2 and HD, Phys. Chem. Chem. Phys. **7**, 1026 (2005).

[7] J. C. Polanyi, Some concepts in reaction dynamics, Acc. Chem. Res. **5**, 161 (1972).

[8] A. Sinha, M. C. Hsiao, and F. F. Crim, Bond-selected bimolecular chemistry: $H + HOD(4\nu_{OH}) \rightarrow OD + H_2$, J. Chem. Phys. **92**, 6333 (1990).

[9] A. Sinha, M. C. Hsiao, and F. F. Crim, Controlling bimolecular reactions: Mode and bond selected reaction of water with hydrogen atoms, J. Chem. Phys. **94**, 4928 (1991).

[10] M. J. Bronikowski, W. R. Simpson, B. Girard, and R. N. Zare, Bond-specific chemistry: OD:OH product ratios for the reactions $H + HOD(100)$ and $H + HOD(001)$, J. Chem. Phys. **95**, 8647 (1991).

[11] M. C. Hsiao, A. Sinha, and F. F. Crim, Energy disposal in the vibrational-state- and bond-selected reaction of water with hydrogen atoms, J. Chem. Phys. **95**, 8263 (1991).

[12] R. B. Metz, J. D. Thoemke, J. M. Pfeiffer, and F. F. Crim, Selectively breaking either bond in the bimolecular reaction of HOD with hydrogen atoms, J. Chem. Phys. **99**, 1744 (1993).

[13] M. J. Bronikowski, W. R. Simpson, and R. N. Zare, Effect of reagent vibration on the $H + HOD$ reaction: An example of bond-specific chemistry, J. Phys. Chem. **97**, 2194 (1993).

[14] K. Liu, Perspective: Vibrational-induced steric effects in bimolecular reactions, J. Chem. Phys. **142**, 080901 (2015).

[15] S. Yan, Y.-T. Wu, B. Zhang, X.-F. Yue, and K. Liu, Do vibrational excitations of CHD_3 preferentially promote reactivity toward the chlorine atom?, Science **316**, 1723 (2007).

[16] W. Zhang, H. Kawamata, and K. Liu, CH stretching excitation in the early barrier $F + CHD_3$ reaction inhibits CH bond cleavage, Science **325**, 303 (2009).

[17] G. Czakó and J. M. Bowman, CH stretching excitation steers the F atom to the CD bond in the $F + CHD_3$ reaction, J. Chem. Am. Soc. **131**, 17534 (2009).

[18] G. Czakó and J. M. Bowman, Quasiclassical trajectory calculations of correlated product distributions for the $F + CHD_3$ $(v_1 = 0, 1)$ reactions using an *ab initio* potential energy surface, J. Chem. Phys. **131**, 244302 (2009).

[19] G. S. Hammond, A correlation of reaction rates, J. Am. Chem. Soc. **77**, 334 (1955).

[20] S. Schlemmer, T. Kuhn, E. Lescop, and D. Gerlich, Laser excited N_2^+ in a 22-pole ion trap: Experimental studies of rotational relaxation processes, Int. J. Mass Spectrom. **185–187**, 589 (1999).

[21] S. Schlemmer, E. Lescop, J. v. Richthofen, and D. Gerlich, Laser induced reactions in a 22-pole trap: $C_2H_2{}^+ + h\nu_3 + H_2 \rightarrow C_2H_3{}^+ + H$, J. Chem. Phys. **117**, 2068 (2002).

[22] O. Asvany, T. Giesen, B. Redlich, and S. Schlemmer, Experimental Determination of the ν_5 Cis-Bending Vibrational Frequency in Ground State $(X^2\Pi_u)$ $C_2H_2{}^+$ using Laser Induced Reactions, Phys. Rev. Lett. **94**, 073001 (2005).

[23] O. Asvany, Padma Kumar P, B. Redlich, I. Hegemann, S. Schlemmer, and D. Marx, Understanding the infrared spectrum of bare CH_5^+, Science **309**, 1219 (2005).

[24] S. Gärtner, J. Krieg, A. Klemann, O. Asvany, S. Brünken, and S. Schlemmer, High-resolution spectroscopy of CH_2D^+ in a cold 22-pole ion trap, J. Phys. Chem. A **117**, 9975 (2013).

[25] S. Brünken, L. Kluge, A. Stoffels, O. Asvany, and S. Schlemmer, Laboratory rotational spectrum of l-C_3H^+ and confirmation of its astronomical detection, Astrophys. J. Lett. **783**, L4 (2014).

[26] S. Brünken, L. Kluge, A. Stoffels, J. Pérez-Ríos, and S. Schlemmer, Rotational state-dependent attachment of He atoms to cold molecular ions: An action spectroscopic scheme for rotational spectroscopy, J. Mol. Spectrosc. **332**, 67 (2017).

[27] S. Thorwirth, P. Schreier, T. Salomon, S. Schlemmer, and O. Asvany, Pure rotational spectrum of CN^+, Astrophys. J. **882**, L6 (2019).

[28] S. Brünken, F. Lipparini, A. Stoffels, P. Jusko, B. Redlich, J. Gauss, and S. Schlemmer, Gas-phase vibrational spectroscopy of the hydrocarbon cations l-C_3H^+, HC_3H^+, and c-$C_3H_2{}^+$: Structures, isomers, and the influence of Ne-tagging, J. Phys. Chem. A **123**, 8053 (2019).

[29] Y. Xu, B. Xiong, Y. C. Chang, and C. Y. Ng, The translational, rotational, and vibrational energy effects on the chemical reactivity of water cation $H_2O^+(X^2B_1)$ in the collision with deuterium molecule D_2, J. Chem. Phys. **139**, 024203 (2013).

[30] O. Asvany, S. Brünken, L. Kluge, and S. Schlemmer, COLTRAP: A 22-pole ion trapping machine for spectroscopy at 4 K, Appl. Phys. B **114**, 203 (2014).

[31] O. Asvany, F. Bielau, D. Moratschke, J. Krause, and S. Schlemmer, Note: New design of a cryogenic linear RF multipole trap, Rev. Sci. Instrum. **81**, 076102 (2010).

[32] O. Asvany, C. R. Markus, T. Salomon, P. C. Schmid, S. Banhatti, S. Brünken, F. Lipparini, J. Gauss, and S. Schlemmer, High-resolution rovibrational spectroscopy of c-$C_3H_2{}^+$: The ν_7 C-H antisymmetric stretching band, J. Mol. Struct. **1214**, 128023 (2020).

[33] C. Western, Pgopher: A program for simulating rotational, vibrational and electronic spectra, J. Quant. Spectrosc. Radiat. Transfer **186**, 221 (2017).

[34] I. R. Sims, Low-temperature reactions: Tunneling in space, Nat. Chem. **5**, 734 (2013).

[35] Y. Georgievskii and S. J. Klippenstein, Strange kinetics of the $C_2H_6 + CN$ reaction explained, J. Phys. Chem. **111**, 3802 (2007).

[36] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, A fifth-order perturbation comparison of electron correlation theories, Chem. Phys. Lett. **157**, 479 (1989).

[37] T. H. Dunning, Jr., Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, J. Chem. Phys. **90**, 1007 (1989).

[38] CFOUR, a quantum chemical program package written by J. F. Stanton, J. Gauss, L. Cheng, M. E. Harding, D. A. Matthews, and P. G. Szalay with contributions from A. A. Auer *et al.* and the integral packages MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see http://www.cfour.de.

[39] M. J. Frisch *et al.*, *Gaussian 16 Revision A.03* (Gaussian Inc., Wallingford, CT, 2016).

[40] See the Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.124.233401 for details regarding the quantum chemical calculations and the kinetic model, which includes Refs. [41,42].

[41] D. J. Cook and R. J. Saykally, Simulated infrared emission spectra of highly excited polyatomic molecules: A detailed model of the PAH-UIR hypothesis, Astrophys. J. **493**, 793 (1998).

[42] P. Virtanen *et al.*, SciPy 1.0: fundamental algorithms for scientific computing in Python, Nat. Methods **17**, 261 (2020).

[43] D. E. Woon and T. H. Dunning, Jr., Gaussian basis sets for use in correlated molecular calculations. V. Core-valence basis sets for boron through neon, J. Chem. Phys. **103**, 4572 (1995).

[44] R. A. Kendall and T. H. Dunning, Jr., Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions, J. Chem. Phys. **96**, 6796 (1992).

[45] W. H. Flygare, Molecular relaxation, Acc. Chem. Res. **1**, 121 (1968).

[46] D. R. Flower, Rotational excitation of HCO^+ by H_2, Mon. Not. R. Astron. Soc. **305**, 651 (1999).

[47] F. L. Schöier, F. F. van der Tak, E. F. van Dishoeck, and J. H. Black, An atomic and molecular database for analysis of submillimetre line observations, Astron. Astrophys. **432**, 369 (2005).

[48] S. Gómez-Carrasco, B. Godard, F. Lique, N. Bulut, J. Kłos, O. Roncero, A. Aguado, F. J. Aoiz, J. F. Castillo, J. R. Goicoechea, M. Etxaluze, and J. Cernicharo, OH^+ in astrophysical media: State-to-state formation rates, Einstein coefficients and inelastic collision rates with He, Astrophys. J. **794**, 33 (2014).

[49] L. González-Sánchez, R. Wester, and F. A. Gianturco, Rotational ‘cooling’ and ‘heating’ of $OH^+(^3\Sigma^-)$ by collisions with He: Quantum dynamics revealing propensity rules under ion trap conditions, Mol. Phys. **116**, 2686 (2018).

[50] W. Federer, W. Dobler, F. Howorka, W. Lindinger, M. Durup-Ferguson, and E. E. Ferguson, Collisional relaxation of vibrationally excited $NO^+(v)$ ions, J. Chem. Phys. **83**, 1032 (1985).

[51] E. E. Ferguson, Vibrational quenching of small molecular ions in neutral collisions, J. Phys. Chem. **90**, 731 (1986).

[52] S. Schlemmer and O. Asvany, Laser induced reactions in a 22-pole ion trap, J. Phys. Conf. Ser. **4**, 134 (2005).

[53] T. Stoecklin and A. Voronin, Vibrational and rotational cooling of NO^+ in collisions with He, J. Chem. Phys. **134**, 204312 (2011).