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Matrix reorganization with intramolecular tunneling of H atom: Formic acid in Ar matrix

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The intramolecular tunneling of hydrogen atom in formic acid HCOOH at low temperatures is considered based on literature experimental data on C–O internal rotation. The energetic and geometric parameters as well as vibrational frequencies for formic acid in cis and trans configurations surrounded by 12 Ar atoms are calculated in the frame of the MP2 approach with extended basis sets. The temperature and pressure dependence of the rate constant is analyzed taking into consideration the matrix reorganization for the Debye model of lattice motion. It has been shown that the available experimental data can be explained by the suggested matrix reorganization mechanism. Theoretical expressions for the temperature dependence of the rate constant agree well with the experimental data on the cis to trans tunneling reactions in formic acid with fitting parameters attaining reasonable values. A mechanism describing pressure dependence of the rate constant for H-atom intramolecular tunneling reactions is also proposed. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3111263]

I. INTRODUCTION

An occurrence of intramolecular tunneling of H atoms at low temperatures had been proved experimentally three decades ago.[1,2] Although attempts to fit the experimental data to a theoretical model for such reactions have been made before,[3] a regular procedure still has not been developed. The reason for that is the necessity to take into account the surrounding matrix which makes this theoretical problem rather complicated. Meanwhile, the H-atom transfer between two molecules[4–8] and from a molecule to a radical[9–12] has been successfully interpreted based on the modified theory of radiationless transitions,[13–15] and a good agreement between theory and experimental data has been achieved (see, for example, Refs. 3 and 13–18).

Recently, two papers[19,20] reported a clearly marked low temperature limit for cis-trans transitions in formic acid (FA) in various noble-gas (Ng) matrices. The conformational state of FA can be efficiently changed by its selective vibrational excitation at low temperatures. Such cis-trans transitions are possible because the *trans*-FA isomer is lower in energy than the *cis*-FA isomer.[21] For this species, the higher-energy cis conformer decays back to the ground state trans structure via a hydrogen tunneling mechanism. The cis to trans tunneling rates of these molecules show remarkable host and temperature effects.

Various mechanisms of the matrix and temperature effects on intramolecular hydrogen tunneling in FA can be expected. In the case of intermolecular H-atom transfer, strong temperature dependence of the rate constant can be due to changes of the reaction barrier due to vibrations of the reagents[13–15] and matrix reorganization as a result of the reaction.[13–15,22,23] It is known that the influence of intermolecular vibrations on the reaction barrier is an important factor in the tunneling rate.[14] Such temperature dependent mechanism of H-atom tunneling affecting its rate constant has been considered in the literature[24–26] (see also monograph 14). Experimental[6–8] and theoretical data for hydrogen tunneling in the fluorene-acridine system have been analyzed on the basis of this mechanism (see, for example Refs. 8, 18, and 27).

As proposed earlier,[28,29] a similar mechanism could be applied to H-atom tunneling in FA. For this, it is necessary to take into account the influence of surrounding atoms on the reagent. The potential barrier for intramolecular tunneling of hydrogen atom can be changed as a result of a weak interaction of Ng atoms with the embedded molecule. On the other hand, the reorganization of the noble-gas lattice due to the intramolecular H-atom transfer may play an essential role in the temperature dependence of the rate constant. The structure of HCOOH changes in the cis to trans rearrangement, which leads to a change of positions of the surrounding particles, resulting in reorganization of the host and making the rate constant temperature dependent. Such

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mechanism for the temperature dependence of the intramolecular tunneling rate constant was suggested in Refs. 28 and 29. The two above mechanisms are examined in Sec. III by quantum-chemical modeling of the influence of the matrix on FA and of the FA molecule on the matrix. The intrinsic structural changes of a molecule such as HCOOH itself should not be important[14] for the temperature dependence of the tunneling rate constant because of large intramolecular frequencies as compared to the cryogenic temperature.

The effects of matrix reorganization on the rate constant of electron transfer were studied first by Marcus for classical media.[30] Then, these effects were considered in detail for the electron and proton transfer in a wide temperature range within the Einstein model of solids.[22,23] In this connection, it is important to take into account two particular features typical for the reactions in Ngs: (i) low frequencies of lattice vibrations and (ii) very low temperatures. The continuous spectrum of lattice vibrations is operative in this case. An expression for the H-atom tunneling rate constant for continuous phonon spectrum including medium reorganization effects has been derived earlier.[13–15,27] Electron transfer in the continuous spectrum has been also studied for a special dispersion law of phonons.[31]

The purpose of the present work is to explain the peculiarities of H-atom tunneling in FA embedded in Ar matrix. First, analytical expressions for the tunneling rate constant accounting for the matrix reorganization effects for a realistic dispersion of phonons, including the Debye phonon spectrum, will be presented in Sec. II based on the results of Ref. 27. The influence of Ar matrix on the barrier for the cis-trans conversion in HCOOH will be studied and the reorganization effects in these processes will be estimated by quantum-chemical calculations. The Ng matrix is modeled by a cluster in which the FA molecule is surrounded by 12 Ar atoms (Sec. III). Modeling of the HCOOH–Ng and Ng–Ng interactions requires computations at a high level of theory taking into account the electron correlation effects. Previously, such calculations were done for the HCOOH–Ar complex[32] with a single Ng atom only. The modeling of influence of the Ng matrix on the properties of embedded molecules is usually performed by using molecular dynamics or molecular mechanics methods (for instance, see Ref. 33 and references therein), where the parameters for interatomic potentials are found by high-level quantum-chemical calculations. Such an approach was applied, for example, for modeling of halogen hydrides in Ar clusters and gave reasonable results.[33,34] This approach seems to be rather promising; however, for more complicated polyatomic molecules the interatomic potentials usually have a rather intricate form. In the future, we plan to test this method for HCOOH embedded in large Ng clusters, but in the present work we limit ourselves to explicit quantum-chemical calculations for the HCOOH–Ar_{12} clusters.

We will show that the model where HCOOH molecule is embedded into a cluster of 12 argon atoms can reproduce the main matrix effects on the tunneling in the cis to trans conversion. The fitting of the calculation results to the experimental data is carried out in Sec. IV.

Temperature and pressure are known to be two important factors affecting tunneling rate constants. By now, experiments were carried out for the temperature dependence only, but experimental studies on the pressure dependence of intramolecular H-atom transfer are likely to be performed soon. Therefore, the problem of the pressure dependence of the rate constant for unimolecular reactions is also addressed in this paper. For instance, we will show that the pressure dependence in the case of intramolecular H-atom transfer differs dramatically from that for the intermolecular transfer.

II. EFFECT OF TEMPERATURE AND PRESSURE ON THE RATE CONSTANT OF INTRAMOLECULAR HYDROGEN TUNNELING

The rate constant of intramolecular H-atom tunneling as a function of temperature and pressure is presented in the double adiabatic approximation[14,15,22] using the theory of radiationless transitions[14,35,36] and accounting for the matrix reorganization. Due to the intramolecular hydrogen transfer the configuration of HCOOH molecule changes, stimulating a rearrangement of the matrix atoms, which corresponds to reorganization of the media.[28,29]

A. Temperature dependence

As mentioned earlier, at very low temperatures the media should be described assuming a continuous phonon spectrum. Based on the results of Ref. 27, the following expression for the rate constant of H-atom transfer for Debye spectrum can be obtained:

$$k = k_{01}\exp\left\{(\Delta E - |\Delta E|)/2kT - E_r/4\hbar\omega_D + \alpha_1 T^4 - \alpha_2 T^5 + O\left(\frac{k_B T}{\hbar\omega_D}\right)^6\right\}, \tag{1}$$

$$\alpha_1 = \frac{7\pi^4}{90}\frac{E_r}{\hbar\omega_D}\left(\frac{k_B}{\hbar\omega_D}\right)^4, \tag{1'}$$

$$\alpha_2 = 60\zeta(5)\frac{E_r}{\hbar\omega_D}\left(\frac{k_B}{\hbar\omega_D}\right)^5, \quad E_r \equiv \frac{\hbar}{2}\sum_\mu \omega_\mu \Delta q^2(\omega_\mu),$$

$$k_B T \ll \hbar\omega_D. \tag{1''}$$

Here, ΔE is the defect of energy, k_B and $\hbar$ are the Boltzmann and Planck constants, respectively, T is the temperature, ω_μ are phonon frequencies, and Δq_μ are the displacements of equilibrium phonon coordinates as a result of the configuration change of the reacting molecule. ω_D is the Debye frequency, which is 65 cm^{-1} for solid argon, ξ is the Riemann zeta function, and E_r is the matrix reorganization energy for the Debye spectrum. The pre-exponential factor k_{01} is proportional to $\exp\{-2S(l)/\hbar\}$; $S(l)$ is the quasiclassical action of the tunneling particle under the barrier:

$$S(l) = \int \{2m_{\mathrm{H}}[U(x) - E_{\mathrm{H}}]\}^{1/2} dx,$$

where $U(x)$ is the potential barrier height in the point x and m_{H} and E_{H} are the mass and the energy of the tunneling

particle. Integration is carried out along the arc l for the region with $U(x) > E_H$.

For an exothermic process ($\Delta E > 0$) the temperature dependence in Eq. (1) is expressed by two terms of the fourth and fifth powers, which are the consequence of the Debye approximation and may change for another dispersion law (see Ref. 15). In the case of an endothermic process ($\Delta E < 0$) the activationlike temperature dependence is added to the exponent. Equation (1) describes the case where the influence of intermolecular vibrations on the reaction barrier is weak. For example, this approximation is valid for intramolecular transformations and electron tunneling in the polar media.

In the high temperature range case the Einstein approximation is applicable for intermolecular vibrations, which gives the well-known Marcus formula[30] for the electron and proton transfer in the classical polar media at $k_B T \gg \hbar\Omega_E/4$:

$$k = k_{02} \exp\left\{-\frac{\alpha_3}{T}\right\}, \quad k_{02} = \frac{1}{\hbar}|V(R_0)|^2 \sqrt{\frac{\pi}{E_r k_B T}}, \tag{2}$$

$$\alpha_3 = \frac{(\Delta E - E_r)^2}{4E_r k_B}.$$

Another way of deriving the Marcus formula in Debye approximation is presented in Ref. 27. As above, this approach is justified for processes involving matrix reorganization induced by intramolecular transformations and the electron transfer in the condensed polar matter. Equations (1) and (2) will be used in Sec. IV for comparison of the theory with the experimental data[19,20] on intramolecular H-atom tunneling.

B. Pressure dependence

Chemical conversions of molecules involving H-atom transfer between reagents in the solid phase strongly depend on the external pressure (see, for example, Refs. 8 and 37–41). A theory for these processes has been developed earlier[8,27,42] and is based on the changes of the phonon frequencies and of the distance between reagents upon the action of pressure. In the case of intramolecular H-atom transfer, the tunneling distance and quasiclassical action in the underbarrier space do not change at reasonable pressures. So, in contrast to intermolecular transfer, the reaction rate constants considered here do not sharply increase upon application of pressure. It is clear that the phonon frequencies and the energy of matrix reorganization, which determine the rate constant of intramolecular reactions, are functions of pressure. In the high temperature range the pressure dependence of the rate constant is concerned with the matrix reorganization.

Let us consider the pressure dependence of the terms in the exponent (1). First of all, it is necessary to find a relation between the tunneling distance and the pressure. Toward this end, for inert matrix it is reasonable to use the parametric Murnaghan equation of state:

$$P = a[\{V_0/V(P)\}^b - 1], \quad V_0 = V(P=0), \tag{3}$$

or

$$V_0/V(P) = (P/a + 1)^{1/b}. \tag{3'}$$

By fitting formula (3′) to the experimental data[43] for argon matrix, it is easy to find the values a and b:

$$a = 3.6 \text{ kbar}, \quad b = 6.4 \quad \text{at } T = 38 \text{ K}$$

and

$$a = 1.6 \text{ kbar}, \quad b = 7.6 \quad \text{at } T = 77 \text{ K}.$$

The influence of pressure on the equilibrium coordinates ξ can be related to the volume change using the following expression:

$$\frac{\xi(P)}{\xi} = \left(\frac{V(P)}{V_0}\right)^{\eta}, \quad \xi = \xi \quad (P=0), \tag{4}$$

where η is a parameter allowing us to take into account a nonuniform compression of the volume, in particular, variable extents of compression for intra- and intermolecular distances (in the case of homogeneous compression, $\eta = 1/3$). Let us introduce the ratio of volumes

$$r = V_0/V(P). \tag{5}$$

Substituting this ratio in the expression (4) and taking into consideration Eq. (3′) one can obtain

$$\xi(P) = \xi\rho^{-\eta} = \xi[(P/a) + 1]^{-\eta/b}. \tag{6}$$

The pressure dependence of the frequency is determined by the expression

$$\Omega(P) = \Omega(V_0/V(P))^{\gamma} = \Omega\rho^{\gamma}, \quad \Omega = \Omega \quad (P=0). \tag{7}$$

Here, $\gamma = -\partial \ln \Omega(P(V))/\partial \ln V$ is the Grüneisen parameter. Taking into account the proportion (5) and Eq. (3′) one can deduce the phonon frequency of the matrix as a function of pressure,

$$\Omega(P) = \Omega(P/a + 1)^{\gamma/b}. \tag{7'}$$

The experimental value of the Grüneisen parameter for argon, measured at frequency $\cong$ 92 K is equal to 2.7 ± 0.1 (Ref. 44) in the vicinity of $T=0$. The Grüneisen parameter does not practically depend on temperature; its deviation at $T=80$ K from the value measured at $T=0$ K is less than 10%.

The energy of media reorganization is determined by the formula (1′). Taking into consideration the relationship $q \sim \xi\sqrt{\omega}$,[14,45] the following expression is found using the formulas (6) and (7′):

$$(\Delta q_\mu(P))^2 = (\Delta q_\mu)^2 \rho^{-2\eta_\mu + \gamma_\mu}, \quad \Delta q = \Delta q_\mu \quad (P=0).$$

With the help of the pressure functions ω_μ and $\Delta q\mu$, it is easy to find the dependence of media energy reorganization on the pressure,

$$E_r(P) = \frac{\hbar}{2}\sum_{\mu} \omega_{\mu}(P)(\Delta q_{\mu}(P))^2$$

$$= \frac{\hbar}{2}\sum_{\mu} \omega_{\mu}(\Delta q_{\mu})^2 \rho^{2\gamma_{\mu}-2\eta_{\mu}}$$

$$= \rho^{2\tilde{\gamma}-2\tilde{\eta}}\frac{\hbar}{2}\sum_{\mu} \omega_{\mu}(\Delta q_{\mu})^2,$$

and finally

$$E_r(P) = E_r\rho^{2\tilde{\gamma}-2\tilde{\eta}} = E_r\left(\frac{P}{a}+1\right)^{(2\tilde{\gamma}-2\tilde{\eta})/b}. \quad (8)$$

Here, $E_r = E_r\,(P=0)$. The sign "~" over a symbol means that a parameter averaged throughout the phonon spectrum is used.

The consideration of pressure dependence of the tunneling rate constant will be restricted at low temperatures by the second and third terms in the exponent (1). As to the high temperature range, the rate constant depends on pressure due to the energy of matrix reorganization (8). The second term in the exponent (1) is independent of temperature and increases with pressure because E_r is a stronger function of pressure than ω_D. Consequently, the position of the low temperature limit of the rate constant moves down upon action of pressure. The temperatures dependent third term in the exponent (1) is the pressure function owing to the dependence of the coefficient α_1 on E_r and ω_D. By substituting the expressions (7′) and (8) in the formula (1) one can get the rate constant of intramolecular transitions at extralow temperatures ($k_BT \ll \hbar\omega_D$),

$$k(P) \sim \exp\left\{\frac{\Delta E - |\Delta E|}{2k_BT}\right\}\exp\left\{-\frac{1}{4}\frac{E_r}{\hbar\omega_D}\rho^{2\tilde{\gamma}-2\tilde{\eta}-\gamma_D} + \frac{7}{90}\frac{E_r}{\hbar\omega_D}\rho^{2\tilde{\gamma}-2\tilde{\eta}-5\gamma_D}\pi^4\left(\frac{k_BT}{\hbar\omega_D}\right)^4\right\}. \quad (9)$$

Using the formula (2) and expressions (7′) and (8), it is easy to find the rate constant of atom transfer at temperatures which comply to the inequality $k_BT > \hbar\omega_D/4$,

$$k(P) \sim \exp\left\{-\frac{1}{4}\frac{(E_r\rho^{2\tilde{\gamma}-2\tilde{\eta}} - \Delta E)^2}{E_r\rho^{2\tilde{\gamma}-2\tilde{\eta}}k_BT}\right\}.$$

Figure 1 demonstrates the pressure dependence of the tunneling rate constant (9) at the following values of the parameters: $E_r = 50\ \text{cm}^{-1}$, $\omega_D = 25\ \text{cm}^{-1}$, $\gamma = 2.7$, and $\eta = 1/3$, in the low temperature range. These values are close to the fitting parameters obtained for the discussed experimental system in Sec. IV. As mentioned above, in contrast to H-atom transfer between molecules, the rate constant of monomolecular reaction decreases when pressure is applied.

III. QUANTUM-CHEMICAL CALCULATIONS OF THE REACTION BARRIER AND MATRIX REORGANIZATION PARAMETERS

The geometric parameters and vibrational frequencies of the cis and trans conformations of FA in the Ar_{12} cluster were calculated by the MP2 method. This approach allows us to estimate the effect of the surrounding and its vibrations on the potential energy surface of the reaction (particularly, the barrier height) and the media reorganization energy ensuing the cis to trans FA transformation.

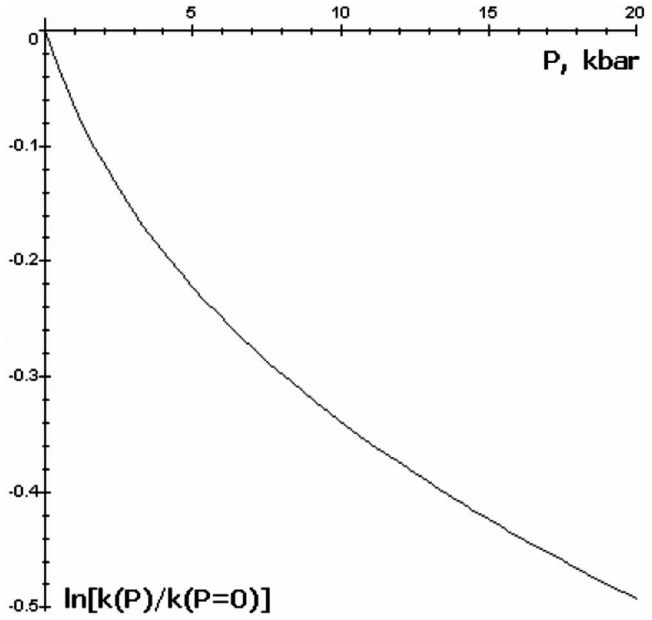

FIG. 1. Calculated pressure dependence of the rate constant at $T = 10$ K.

A. Computational details

Solid Ngs (except helium) have a face-centered-cubic lattice[46–48] with 12 neighbors around each atom. Therefore, we consider an HCOOH molecule embedded into an Ar_{12} cluster constituting the first solvation shell. This system corresponds to a single-substitution site and represents a smallest cluster appropriate for modeling of HCOOH in a Ng matrix. Calculations of such clusters at the most common density functional level of theory (e.g., B3LY/6-31G*) is not difficult. However, the Ng–Ng and Ng–HCOOH interactions are governed mainly by the dispersion effects, and hence, the use of higher-level electronic correlation methods, such as the MP2, MP4, or CCSD, with flexible basis sets containing polarization and diffuse functions is required to produce adequate results. The higher-level studies are more computationally demanding, and a balance needs to be found between available resources and reasonable accuracy.

We start with modeling the Ng–Ng interactions at the MP2 and MP4(SDTQ) levels with different basis sets (Möller–Plessett perturbation theory up to the second and fourth orders with account of single, double, triple, and quadruple excitations). The calculations were carried out with the GAUSSIAN-03 program package.[49] From the experimental data,[46] one can estimate the Ar–Ar equilibrium distance as 3.72 Å with the interaction energy of 52 cm^{-1}. A scan of the potential energy curve along the Ar–Ar distance in the Ar_2 dimer shows that the results by the MP2 and MP4 methods are similar and the simpler MP2 method is therefore quite suitable to describe the Ar–Ar interactions. Calculations with the extended aug-cc-pVTZ basis set[49–51] (valence triple-zeta augmented by diffuse and polarization functions, APVTZ)

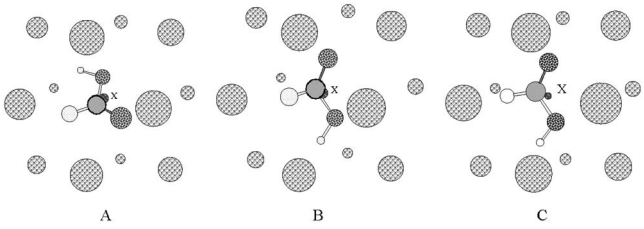

FIG. 2. Different orientations of HCOOH (cis) in Ar matrix; *X* is the center of the cell.

give a minimum on the Ar_2 potential curve at R_e=3.8 Å, but the calculated interaction energy, 112 cm^{-1}, is overestimated.

The basis set superposition error (BSSE) correction leads to the interaction energy of ~84 cm^{-1}, which is in a better agreement with experiment. A removal of the diffuse functions from the basis set (PVTZ) leads to substantial underestimation of the Ar–Ar interaction. A smaller double-zeta aug-cc-pVDZ (APVDZ) basis set with diffuse functions produces more accurate results (3.95 Å and 52 cm^{-1}). However, even the MP2/APVDZ approach is too cumbersome to be applied for the model system under investigation. The calculations can be simplified by replacing the core electrons by pseudopotentials with a suitable coreless basis set for heavy atoms. For this purpose, we tested the LanL2 pseudopotential[49,52–54] with the corresponding double-zeta basis set augmented by diffuse and polarization functions taken from aug-cc-pVDZ (LanL2apDZ). This approach appears to be quite reasonable for reproducing the equilibrium distance (R_e~3.8 Å), but the Ar–Ar interaction energies are significantly overestimated before considering BSSE but underestimated after the BSSE correction is included (180 and 14 cm^{-1}). Hence, we can use the MP2/LanL2apDZ method for geometry optimization, but the energy values should be refined with more flexible basis sets. Additionally, the MP2/LanL2apDZ approach was tested for the Ar_{13} cluster. In this case, the calculated Ar–Ar distance between the central atom and its neighbors is 3.706 Å, in good agreement with experimental value for solid Ar, 3.717 Å.[46]

At the next stage, the suggested theoretical approaches were examined for their ability to properly describe the Ar–HCOOH interaction. The Ar–HCOOH calculation results[32] obtained at the MP2/6-311++G(2*d*,2*p*),6-311+G(3*df*) ×[Ar] level of theory were used as a benchmark. In the most stable Ar–HCOOH geometric structure, the Ar atom is located approximately along the O–H bond with the Ar–H distance and interaction energy of 2.63 Å and 133 cm^{-1}, respectively. The geometry optimization for this configuration was performed at the MP2 level with the basis set designated below as B2, which includes APVDZ for O, C, and H atoms and LanL2DZap for the Ar atom. The optimization resulted in approximately the same structure of the complex as that in Ref. 32 but with a slightly shorter Ar–H distance (2.55 Å). The interaction energy with the BSSE correction at this level of theory was found to be 73 cm^{-1} but with a larger and more flexible B3 basis set (APVDZ at Ar and APVTZ at O, C, H) the result is 132 cm^{-1}, in good agreement with the value from Ref. 32. Based on these results, one can conclude that the MP2/B2 level is suitable for geometry optimization of the system under investigation, but the energy values should be refined with the more sophisticated B3 basis set.

Next, we tested the chosen method for description of molecular properties of *trans*- and *cis*-HCOOH. The transition state (TS) between the two isomers can be found by rotation of the OH group around the C–O axis. The FA conformers and the TS (barrier) between them were calculated at the MP2/APVDZ and MP2/APVTZ levels. The calculated molecular properties (geometric parameters, vibrational frequencies, and relative energies) are in good agreement with the results of other high-level calculations and the available experimental data,[32,55–57] with deviations of ~0.01 Å for bond lengths, 0.2°–0.3° for bond angles, 0.5%–1% for vibrational frequencies, and ~0.5% for the barrier height and cis-trans isomerization energy. Moreover, there is no substantial difference between the relative energies of the cis, trans, and TS structures calculated with the APVDZ and APVTZ basis sets. Therefore, the theoretical approaches used in the current work are suitable for describing the HCOOH conformational change.

B. HCOOH in the Ar_{12} cluster

It is probable that the HCOOH molecule can have several different orientations in a Ng matrix. At least two matrix sites were distinguished by the IR spectroscopy.[19] We tried to find different orientations of HCOOH in an Ar_{12} cluster computationally. Initially, the Ar positions were kept frozen as in the Ar_{13} cluster, whereas the HCOOH coordinates were optimized. Three different positions of FA in the argon cluster were found (Fig. 2). In geometries *A* and *B*, the embedded molecule is located along the main diagonal of the Ar_8 cube,

TABLE I. Geometric parameters of cis and trans isomers of FA as an isolated molecule and inside the Ar_{12} cell optimized at the MP2/B2 level of theory. The B2 basis set includes LanL2DZap for Ar and APVDZ for O, C, and H. The bond lengths are given in Å and bond angles in degrees.

	R(CO)	*R*(CO′)	*R*(CH′)	*R*(OH)	φ(O′CO)	φ(H′CO)	φ(HOC)	τ(HOCO′)
				trans				
Isolated	1.358	1.215	1.103	0.975	125.1	109.5	106.3	0.0
Inside Ar_{12}	1.354	1.216	1.098	0.975	125.0	109.8	106.5	0.0
				cis				
Isolated	1.365	1.209	1.109	0.970	122.2	113.7	108.7	180.0
Inside Ar_{12}	1.360	1.210	1.103	0.970	122.0	113.8	108.5	180.0

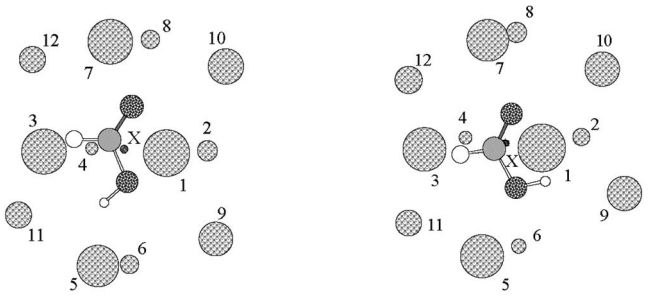

FIG. 3. Optimized *C* configurations of the HCOOH@Ar_{12} system (cis and trans isomers); *X* is the center of the system.

but it has a different orientation relative to the cube vertices: in the *A* structure the C=O bond is directed approximately toward the cube vertex and in the *B* structure this bond is positioned near the cube face. In structure *C*, HCOOH is parallel to two opposite Ar_8 cube faces (see Fig. 2). All these configurations have C_s symmetry. Configuration *C* is the most stable and therefore it was used in further calculations; the *A* and *B* structures lie ~1350 and ~600 cm^{-1} higher than *C* in energy.

The geometry optimization of the HCOOH–Ar_{12} systems shows that the Ar matrix has only negligible influence on the HCOOH geometry in comparison with the isolated molecule (Table I). This effect may be more significant for molecules, which interact with the matrix more strongly, as in the case of H bonding. On the other hand, the Ar_{12} cage is substantially distorted due to the interaction with HCOOH. After geometry optimization, the Ar atoms located in an equatorial position relatively to the C=O bond (denoted as 1–4 in Fig. 3) are shifted toward the center of the cluster, and the others (5–12) are displaced in the opposite direction (Fig. 3, Table II). The shifts are significant (up to 0.5–0.7 Å) mainly for the "equatorial" Ar atoms, which are attracted to the HCOOH molecule. This means that the effective size of the HCOOH molecule does not differ significantly from the "size" of an Ar atom: for FA the cage becomes slightly larger along the C=O bond and smaller in the orthogonal directions. Finally, the distortion of the Ar lattice by the FA molecule would lead mainly to a compression of the first coordination shell around the impurity with gradual attenuation of deformations in the next layers. In a larger system, the deformation of the Ar_{12} cage should be smaller than in the present model due to attractive influence of the outer shells. Nevertheless, the main trends are expected to be the same because the Ar–HCOOH interactions are substantially stronger than the Ar–Ar interaction (132 and 52 cm^{-1}, respectively, at the MP2/B3 level with BSSE correction).

The vibrational analysis revealed one imaginary frequency of ~3 cm^{-1} for *cis*-HCOOH in the Ar_{12} cluster. Reoptimization of this configuration along the coordinates corresponding to this vibration produced a very similar structure but with C_1 symmetry. There were no imaginary frequencies in this configuration, but the energy decrease was negligibly small (~0.6 cm^{-1}). The most probable reason for this symmetry lowering is accumulation of small numerical errors during calculations of a very large number of molecular integrals. Keeping this in mind, the C_s-symmetric configuration was used for further investigations.

For the HCOOH–Ar_{12} system, the calculated frequencies are clearly separated into three groups: (1) internal vibrations of HCOOH (with frequencies similar to those in the isolated molecule), (2) six vibrations of HCOOH as a rigid body inside the Ar_{12} cluster with frequencies from 200 to 90 cm^{-1}, and (3) vibrations of the Ar atoms below 60–40 cm^{-1} (see Table III).

C. Potential energy of the cis-trans HCOOH conversion in the Ar_{12} cluster

According to the adiabatic approximation, tunneling of H atom occurs much faster than the displacement of the heavier particles. Thus, the surrounding atoms during the tunneling process occupy their optimized positions for the initial or final state. This approximation was successfully applied earlier for the hydrogen-atom tunneling between two molecules.[18] The corresponding energy barrier of the H-atom transfer from fluorene to acridine molecule is markedly lower in the optimized configuration.

In the case of the cis-trans HCOOH conversion, the potential energy surfaces were calculated for five configurations of the molecule and Ar_{12} cluster (see Table IV):

(1) isolated molecule in cis configuration;
(2) molecule in cis configuration inside the Ar_{12} cluster with Ar atomic positions taken from Ar_{13} and frozen [Fig. 2(c)];
(3) molecule in cis configuration inside optimized Ar_{12} cluster;
(4) isolated molecule in trans configuration;
(5) molecule in trans configuration inside optimized Ar_{12} cluster.

The exponential factor for the tunneling process $\{-2S(l)/\hbar\}$ is calculated for each profile at $E_H=E(\text{cis})$. The results of the potential energy surface scan show a moderate effect of the Ar_{12} cage on the barrier characteristics. For the cis form, embedding HCOOH into an Ar_{12} cluster leads to a growth of the barrier height and exponential factor, especially after cluster optimization—by up to 5% and 3%. The

TABLE II. Distances from the center of the model cell to Ar atoms [$R(X-Ar_n)$, in Å] for cis and trans isomers of HCOOH in the Ar_{12} model cluster (shown in Fig. 3).

	n							
	1, 2	3, 4	5, 6	7, 8	9	10	11	12
cis	3.16	3.52	4.21	3.94	3.97	3.82	4.03	3.88
trans	3.30	3.50	4.20	3.87	4.04	3.85	3.95	3.62

TABLE III. Calculated vibrational frequencies (cm^{-1}) for cis and trans isomers of FA inside the Ar_{12} cluster.

	trans		cis	
Assignment	Isolated	In Ar_{12}	Isolated	In Ar_{12}
O–H stretching	3728 a'	3721	3790	3791
C–H stretching	3138 a'	3193	3052	3111
C=O stretching	1772 a'	1775	1805	1805
HCO bending	1396 a'	1411	1404	1422
HOC bending	1295 a'	1305	1274	1278
C–O stretching	1116 a'	1124	1097	1120
HCOO torsional	1047 a''	1068	1020	1032
HOCO torsional	673 a''	683	525	527
OCO bending	618 a'	624	643	649
		202, 118 116, 105		220, 126 114, 110
FA librations and rotations inside the Ar_{12} cluster	None	103, 90	None	108, 94
		62, 61, 59, 58,		62, 60, 60, 59,
		56, 54, 53, 51,		57, 55, 48, 48,
		48, 44, 43, 41,		43, 43, 42, 39,
		38, 36, 36, 35,		36, 35, 34, 33,
		31, 31, 29, 29,		32, 31, 30, 29,
		28, 25, 24, 24,		26, 26, 24, 22,
		21, 20, 17, 15,		22, 18, 15, 15,
Vibrations of the Ar_{12} cluster	None	12, 9	None	8, 3i

variations are smaller with the Ar coordinates taken from crystalline positions, but they exhibit the same trend. For a real system one can expect intermediate results, i.e., the presence of the outer layers around the first Ar shell will reduce the atomic displacements in this shell. For trans configuration the cluster influence is opposite—it leads to lowering of the barrier height and exponential factor by ~3% and 6%, respectively. So, the Ar atoms from the first solvation shell around the FA molecule do not create an obstacle for OH rotation around the C–O axis—the proton passes by the nearest Ar atoms without experiencing substantial repulsion.

Next we discuss the influence of matrix vibrations on the reaction barrier, which was modeled for the HCOOH-Ar_{12} system in the following way:

(1) The atomic displacements along the vibrational coordinates in the positive and negative directions ($s+$ and $s-$) were calculated for each mode of the Ar_{12} cluster. The displacement value for each vibration was taken equal to the amplitude of the first excited vibrational state ($n=1$).
(2) The potential energy surface for the cis-trans conversion of HCOOH–Ar_{12} was scanned for each set of geometric parameters of the Ar cage with the applied atomic displacements due to vibrations.

It was found that all vibrations of the cluster (from 62 to 8 cm^{-1}) have a weak influence on the potential curve of the H-atom transfer. The variations of the barrier height do not

TABLE IV. Adiabatic energy profiles (cm^{-1}) and exponential factors $\sigma=2S(l)/\hbar$ for the HCOOH cis-trans conversion calculated at the MP2 level with the basis set including LanL2DZap for Ar and APVTZ for O, C, and H. Zero energy corresponds to the cis configuration.

τ[a]	Isolated cis	Ar_{12}-frz[b] cis	Ar_{12}-opt[c] cis	Isolated trans	Ar_{12}-opt[c] trans
180	0	0	0	0	0
165	198	202	195	198	187
150	751	731	729	752	689
135	1536	1440	1487	1543	1373
120	2350	2187	2319	2364	2120
105	2956	2840	3012	2961	2775
90	3138	3156	3287	3103	3031
75	2794	2910	2970	2682	2662
60	1982	2135	2146	1762	1752
45	907	1086	1075	569	572
30	−152	59	25	−597	−602
15	−919	−687	−745	−1437	−1497
0	−1201	−962	−1029	−1742	−1840
σ	45.70	46.59	47.06	44.58	43.14

[a]τ is the torsional HOCO′ angle in degrees.
[b]Coordinates of Ar atoms are frozen in the crystalline positions.
[c]Optimized for cis or trans isomers.

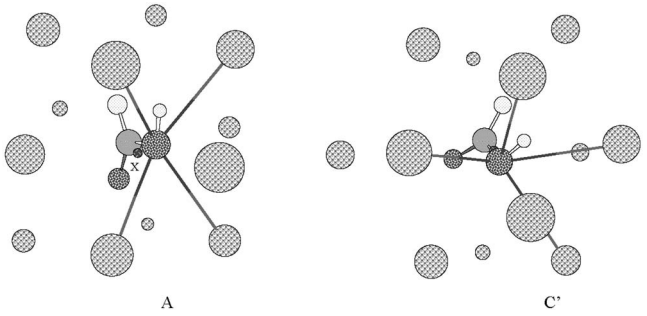

FIG. 4. Optimized *A* and *C′* configurations for the cis isomer of the HCOOH @ Ar_{12} system.

exceed 0.2%–0.4%, especially for the lowest frequencies, which can be activated at low temperatures. The estimated variations of the exponential factor under maximal displacements of the vibrating atoms are in the range of ±0.1%–0.2%; only for a few cases these variations measure up to 0.3%–0.4%. One has to keep in mind that these variations take place for maximal atomic displacements in the vibrationally excited states. Moreover, they have opposite signs with almost equal absolute values of opposite shifts at the same vibration, and hence the contributions from their variations will partially cancel one another. Thus, the mean effect will be much weaker. Within the theoretical approach applied here, the Ar–HCOOH interaction energies are overestimated, and so more accurate calculations would result in an even weaker influence of the host on the reaction barrier. Thus, the vibrations of the Ar_{12} cluster do not change substantially the height and form of the potential barrier for the hydrogen tunneling reaction.

It is possible that a rather moderate influence of the Ar_{12} cluster on the barrier of HCOOH conversion owes to the selected conformation and for some other arrangements of HCOOH in the Ar_{12} cage, the surrounding Ar atoms can hinder the H movement along the cis-trans path. In order to verify this, we investigated two additional structures where the tunneling path takes the H atom to shorter distances from some of Ar atoms. Structure *A* was considered first (Fig. 2), where the proton tunnels through the O–Ar contact (Figs. 2 and 4). The other configuration (structure *C′* in Fig. 4) was built from structure *C* by reorientation of the HCOOH molecule in the cage. The energies of the optimized structures *C* and *C′* are almost the same, whereas configuration *A* is ~500 cm^{-1} higher in energy. Additionally, the nonsymmetrical configuration C_1 discussed above was also tested.

For all these structures, the potential energy profiles for H motion from cis to trans configuration are similar: for configuration *A* the barrier height becomes ~1.8% higher than that for the previously discussed structure *C*; for C_1 and *C′* configurations these deviations are less than 1% (Table V), even if the moving H atom passes almost through the O–Ar line at a distance of ~2.4 Å from the Ar atom. Thus, with other HCOOH orientations in the Ar cage we should observe the same trends for the barrier heights and exponential factors as for the *C* configuration. Due to the similarity of the barrier properties for these configurations, one can expect similar influence of the matrix vibrations on the barrier properties—similarly weak as for the *C* configuration discussed above. This should result in a small temperature effect on the barrier, and the observed temperature dependence of the cis to trans HCOOH reaction rate in an argon matrix should therefore originate from some other mechanisms.

It is worth noting that these evaluations were made for comparative purposes with the middle-size B2 basis set. Calculations with a larger basis set including APVTZ at O, C, and H atoms give lower barrier heights of ~100 cm^{-1} (see the appropriate data in Tables IV and V). These differences in the barrier values lead to variations of sigma factors in the range of 1.5%.

Another factor which may affect the temperature dependence of the rate constant is matrix reorganization. It occurs if the system after tunneling appears in an unrelaxed geometry. The tunneling rate would increase if the *cis*-FA @ Ar_{12} system can be thermally modified to the geometry which is optimal for the *trans*-FA @ Ar_{12} system. We estimated various components of the reorganization between the optimized *cis*-FA @ Ar_{12} and *trans*-FA @ Ar_{12} configurations. For this purpose the following computational steps were performed:

(1) The energy of the trans isomer after hydrogen tunneling from the cis form was calculated. In this case, the HOCO torsional angle was equal to zero, but the interatomic distances, bond angles, HCOOH orientation, and Ar atom positions were as in the initial cis configuration.
(2) Internal parameters of HCOOH (interatomic distances and bond angles) were optimized, but its position in the Ar_{12} cluster and the coordinates of Ar atoms were fixed.
(3) The position of HCOOH in the cluster was optimized; only Ar coordinates were fixed.
(4) The coordinates of Ar atoms were optimized.

TABLE V. Adiabatic potential energy profiles (cm^{-1}) for the cis-trans H tunneling in FA for different initial configurations calculated at the MP2 level with the basis set including LanL2DZap for Ar and APVDZ for O, C, and H.

	τ(HOCO′)						
	180°	150°	120°	90°	60°	30°	0°
Isolated FA	0	773	2420	3250	2323	−110	−1194
C, C_s	0	792	2493	3393	2293	110	−971
C, C_1	0	782	2488	3403	2319	124	−973
C′, C_s	0	784	2741	3410	2300	165	−854
A, C_s	0	821	2566	3456	2336	123	−961

TABLE VI. Reorganization energies (cm^{-1}) of *trans*-HCOOH inside the Ar_{12} cluster after tunneling from the cis isomer calculated at the MP2 level in configuration *C*.

	Ar, B2[a]	Ar, B3[b]	Ar, B3[b,c]
Full (Ar_{12}+FA)	396	353	364
FA inner	272	249	263
Ar_{12} and FA position	124	104	101
FA position	62	64	58
Ar_{12} only	62	40	43
EDCT[d]	1376	1373	1334

[a]The B2 basis set includes LanL2apDZ for Ar and aug-cc-PVDZ for O, C, and H.
[b]The B3 basis set includes aug-cc-PVDZ for Ar and aug-cc-PVTZ for O, C, and H.
[c]BSSE-corrected energy.
[d]EDCT is the energy difference between the cis and trans isomers.

The differences of the energies calculated in these four steps give estimates of the energy components corresponding to relaxation of the HCOOH bonds and bond angles (FA inner; step 2-step 1), reorientation of HCOOH in the cluster (FA position; step 3-step 2), and reorganization of Ar atoms (Ar_{12} only; step 4-step 3). The components of the reorganization energy and the energy difference between the optimized cis and trans isomers (EDCT) are presented in Table VI. It follows from these results that the EDCT value for HCOOH–Ar_{12} is smaller than for isolated HCOOH (1334 and 1484 cm^{-1}, respectively, at the MP2/B2 level). This is explained by a stronger interaction of *cis*-FA with the Ar_{12} cluster compared to *trans*-FA as discussed elsewhere.[37]

The total reorganization energy is ~350–400 cm^{-1}, and the main contribution is the "FA-inner" component, which originates from the reorganization of HCOOH bond angles and distances. The contributions of reorientation of HCOOH in the cluster (FA position) and the reorganization energy of the Ar_{12} cluster are substantially smaller. These values are slightly lower with the more flexible B3 basis set, but the picture remains similar and the BSSE correction is not important. For intramolecular rearrangements, such as internal rotation, the mutual contributions of the basis sets from different parts of the system are similar for different configurations, and hence the BSSE correction has only a weak effect on their relative energies.

IV. FITTING OF THEORY TO EXPERIMENTAL DATA

Now we are in position to compare experimental[19,20] and theoretical data for the temperature dependence of the rate constant of the cis to trans HCOOH conversion in an Ar matrix. As shown in Refs. 14 and 58, at low temperatures, where both reorganization of the matrix and H-atom transfer are quantum phenomena, the expression (1) is valid for the rate constant description. According to inequality (1″), Eq. (1) is applicable for the fitting procedure to the experimental data[19,20] in the interval where the lower limit is 4.2 K and the upper limit is in the vicinity of ≈15 K.

At elevated temperatures, the experimental data demonstrate the Arrhenius behavior for the rate constant starting from $T=17$ K. Therefore, the whole high temperature range ($17<T<35$ K) is described by formula (2), which is correct at $T>\hbar\Omega_E/4k_B\approx 15$ K. This range corresponds to the classical media reorganization and quantum H-atom transfer.

It follows from Eqs. (1′) and (2) that the five fitting parameters k_{01}, k_{02}, α_1, α_2, and α_3 can be expressed using the values of ΔE, E_r, and $\omega_D(W_E)$. The absolute value of the tunneling rate constant is difficult to calculate accurately. Even a small inaccuracy of 5%–10% in the determination of barrier parameters would produce a dramatic error (orders of magnitude) for the absolute value of the rate constant.[58] Thus it is reasonable to determine the tunneling system parameters only for the temperature dependence of the rate constant. In addition, we can restrict ourselves by the term $\sim T^4$ in the exponent (1) for the fitting procedure, because this term plays the main role at low temperatures. In other words, the values α_1 and α_3 will be investigated.

Let us consider first the results of quantum-chemical calculations. The released energy is in the range of 1334–1376 cm^{-1} (Table VI). This energy significantly differs from the defect of energy, so a fraction of the released energy transfers to excitation of a suitable intramolecular mode of FA in the final state. After penetration through the barrier all atoms have zero velocities, and hence vibrations can be activated only due to the geometry difference between the postbarrier and final states. But as mentioned above, the system has the same symmetry in the initial, postbarrier, and final states, and the geometry displacement in this case belongs to the fully symmetric a' irreducible representation of the C_s point group. Therefore, only a' vibrations may be activated. For the cis-trans transition, alterations of geometric parameters are substantial for bond angles, especially for HCO and OCO (Table I). However, the frequency of HCO bending is too high (Table III), and the most convenient vibration to be excited in connection with the H-atom transfer is the OCO bend. Two vibrational quanta should be excited in this case. Nevertheless, it is possible that in some cases the HOC vibration will also be activated, and redistribution between the activated OCO and HOC vibrations can occur. Taking into account the anharmonicity of vibrations, a rough estimation gives for the energy of the OCO second excitation level the value approximately equal to 1176 cm^{-1}. Consequently, the magnitude of ΔE is in the range of 158–200 cm^{-1}.

The reorganization energy modeled with the Ar_{12} cluster is in the range 40–62 cm^{-1} (Table VI), and the frequencies of intermolecular vibrations of the reaction system $\omega_D(\Omega_E)$ are 62–220 cm^{-1} (Table III). At the considered temperatures HCOOH librations and rotations in the Ar_{12} cluster are frozen; therefore it is reasonable to take into account only the vibrations of the cluster with the calculated $\omega_D=62$ cm^{-1} close to the experimental value. The real phonon spectrum[45] is more complicated in comparison with those in the Debye or Einstein models of solids. So, we will use the effective frequency ω(eff) as a fitting parameter instead of Debye or Einstein frequencies.

On the other hand, the fitting curve plotted by interpolation of formulas (1′) and (2) with parameters $\alpha_1=3.5\times10^{-5}$ cm^4 and $\alpha_3=59$ cm^{-1} is presented in Fig. 5. Let us analyze the values of the system parameters, obtained as the

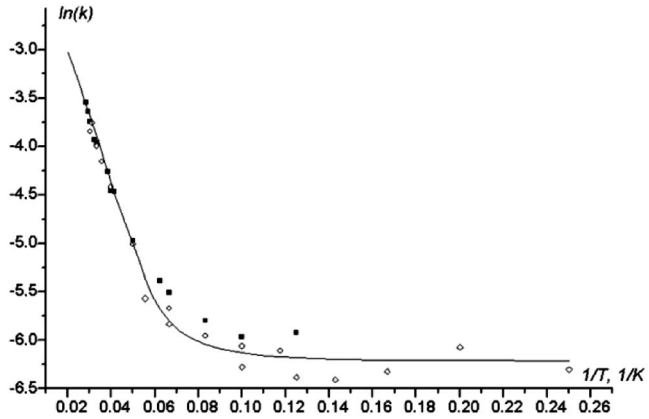

FIG. 5. The temperature dependence of the rate constant of hydrogen tunneling in the HCOOH@Ar_{12} system for the cis to trans HCOOH conversion in Ar matrix. The points are the experimental data (Refs. 19 and 20) and the solid curve is the result of fitting of the theoretical temperature dependence to the experimental one.

result of the fitting procedure. According to Eqs. (1′) and (2) and computed values of parameters α_1 and α_3, there are two equations to determine ΔE, E_r, and ω(eff),

$$3.5 \times 10^{-5}\ \text{cm}^4 = \left\{ \frac{7\pi^4}{90} \frac{E_r}{\hbar\omega_D} \left(\frac{k_B}{\hbar\omega_D} \right)^4 \right\},$$
$$59\ \text{cm}^{-1} = (\Delta E - E_r)^2 / 4E_r k_B. \tag{10}$$

Starting from the quantum-chemically calculated interval for E_r=40–62 cm^{-1}, it is easy to find from equalities (10) ΔE =137–183 cm^{-1} and ω(eff)=24.4–26.7 cm^{-1}. It is clear that the fitting parameters E_r, ΔE, and ω(eff) satisfy both Eqs. (1) and (2). Compare the value of ΔE with the permissible range for this parameter and substitute it in Eq. (10); it is then possible to find finally ΔE=158–183 cm^{-1}, E_r =50–62 cm^{-1}, and ω(eff)=25.5–26.7 cm^{-1}. It is easy to see that all values of the fitting parameters lie within the intervals determined quantum chemically and are physically reasonable.

As to the stability of the fitting parameters ΔE, E_r, and ω(eff) with respect to the accuracy of quantum-chemical calculations, let us assume that the accuracy of these values is 10%. In this case, instead of the considered intervals one can find ΔE=143–194 cm^{-1}, E_r=43–68 cm^{-1}, ω(eff) =24.8–27.2 cm^{-1}. All these values are also inside the calculated intervals. The magnitude of ω(eff) is significantly lower than the Debye frequency (see D-atom tunneling in HD crystal[12,15,58]). This may be caused by the complexity of the real phonon spectrum.[45]

V. CONCLUSIONS

Intramolecular tunneling of hydrogen atom at low temperatures is studied based on quantum-chemical calculations, with the purpose to explain the temperature dependence of the tunneling dynamics. The tunneling rate constant depends on the energy of media reorganization, energy defect of the intramolecular subsystem, frequencies of intermolecular oscillations, and height and width of the potential barrier of the reaction. The MP2 method with extended basis sets provides these parameters for the experimentally investigated system of FA embedded in solid argon.[28,29] The geometric parameters and vibrational frequencies for FA in the cis and trans configurations surrounded by 12 Ar atoms were computed. This surrounding and its vibrations do not change much the geometric structure, potential energy profile, and reaction barrier height, with alterations of all of these parameters not exceeding 1%. Quite to the contrary, the change of the FA configuration as a result of the H-atom transfer substantially affects the matrix. Displacements of the surrounding Ar atoms reach 0.7 Å. It follows that the most probable reason for the observed temperature dependence is the matrix reorganization. Based on the variation of these matrix parameters under pressure, the pressure dependence on the rate constant of intramolecular H-atom transfer is also presented. It is shown that this dependence differs strongly from the previously described rate constant pressure dependence in the case of intermolecular H-atom transfer.

The theoretical and experimental data allow us to suggest the following mechanism of the rate constant temperature dependence.[28,29] The configuration of the molecule changes upon the intramolecular transition, and this stimulates the reorganization of the environment. This reorganization results in the temperature dependence of the rate constant. The continuous phonon spectrum was carefully considered in the range of low temperatures. We used the expressions for the rate constant of intramolecular conversions in Debye approximation for the lattice motion taking into account the media reorganization. The theoretical expressions for the temperature dependence of the rate constant were compared with the experimental data. As a result, the theory properly describes the experimental data with reasonable values of the fitting parameters.

There are many similar unimolecular reactions, and the method developed here represents a reliable basis for their studies and for comparison of theoretical and experimental data. Quantum-chemical calculations with larger model clusters will allow one to substantially increase the accuracy of theoretical predictions for the reorganization energy in such systems.

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